Effect of Alkali-NaOH Pretreatment on Methane Production from Anaerobic Digestion of Date Palm Waste

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ABSTRACT

Anaerobic digestion of the date palm empty fruit bunch is a promising technology for both solid waste management and biogas production. The date palm empty fruit bunch is a lignocellulosic waste that takes more time for degradation and has a low biodegradability, thus pretreatment is needed to improve anaerobic biodegradation. In this study, the substrate was pretreated with different ratios of alkali-NaOH: 6, 18 and 30% (w/w) (ratio weight of NaOH / weight of Volatile Solid) for 10 min at room temperature to evaluate the effect of high alkali concentration on the methane potential and biodegradability. The experiment was conducted in a 5 L batch reactor under mesophilic conditions (37 °C). The methane potential of the untreated substrate was 98.5 N mL/gVS. The best methane potential improvement of 104% was achieved in the treatment of 18% (w/w) (204 N mL/gVS) with a biodegradability of 50%. Besides, two kinetic models were used to fit the experimental methane potentials and to explore process parameters (Modified Gompertz and Transference function). The best fit for predicting the parameters of methane production was observed for the 18% (w/w) pretreatment using the transference function, with a maximum methane production rate of 5 N mL/gVS.d.

Keywords: Alkali Pretreatment; Methane; Biogas; Date Palm Empty Fruit Bunch; Kinetic Study.

INTRODUCTION

The date palm tree (Phoenix dactylifera L.) represents a large area in arid and semi-arid regions, considering their nature in resisting the high temperature and lack of water existence. In 2019, the area of the date palm in the Drâa region was 45,892 Ha, 77% of the total area in Morocco, with a production of 78,540 t (Moroccan Ministry of Agriculture, 2019). In the arid and semi-arid areas, date palm waste represents the main quantity against the total waste quantity of the region. In general, the amount of waste that can be produced from each date palm tree is around 20 kg of waste yearly (Chandrasekaran and Bahkali, 2013). These wastes are in general used for feeding cattle (Chehma and Longo, 2001), or burning in random ways leading to environmental problems. Burning these wastes could produce household air pollution, which is responsible for the death of about 3.8 million people around the world each year (WHO, 2018). The valorization of date palm waste can contribute to increase the social and economic positive impact on the population of this area.

Several techniques are used for treating wastes such as biological, chemical and physical processes. Anaerobic digestion (AD) is one of the biological processes that treat organic wastes, by degrading organic matter with a microbial ecosystem operating in the absence of oxygen (Karouach et al., 2021), and also resulted in waste

reduction. The AD process produces two main products, the first one is biogas, which contains mostly methane and CO_2 (Beniche et al., 2020), and the second one is digestate which contains a large quantity of organic matter that cannot be fully degraded and can be used as a fertilizer in agriculture use (Juanga-Labayen et al., 2021). The biogas is considered as a renewable energy which does not produce air pollutants, nuclear waste or ashes (Lo et al., 2019). AD can help reduce the fires in the oasis each year that causes great damage to date palm farms.

The date palm waste, which contained lignin, cellulose and hemicellulose, could be used in biological processes (Chandrasekaran and Bahkali, 2013). The lignocellulosic wastes are considered as suitable feedstock for bioenergy generation with the ability of cellulose and hemicellulose on converting to monosaccharides after hydrolysis (Kainthola et al., 2019). The lignocellulosic materials are complex and make the degradation difficult in AD. Few studies on producing biogas from date palm waste were discussed in the literature. In a recent study, the experimental methane yield from date palm empty fruit bunch (DPEFB) using continuous stirred tank reactor (CSTR) under mesophilic conditions was 118.5 NmL/gVS with a biodegradability of 39% (Lahboubi et al., 2020). Nevertheless, the production of biogas or methane can be improved by increasing the solubility of organic matter during the anaerobic digestion process (Wong et al., 2018). Different pretreatments were used in order to improve biodegradability and methane production, such as physical, chemical and biological (Bernat et al., 2020). The use of the pretreatment stage is to improve the physical accessibility of lignocellulosic matter to microbes (Karouach et al., 2020) and modify the structure of cellulosic materials, which are complex, with decreasing degree of polymerization, weakening of the lignin and carbohydrates bonds and increased surface area of particles (Mudhoo, 2012). In literature, most researchers approve that the alkali pretreatment appears to be the most effective method in terms of breaking the ester bonds between lignin, hemicellulose and cellulose (Khadaroo et al., 2019). The alkali pretreatment increases the digestibility of cellulose and results in the removal of hemicellulose and lignin materials from lignocellulosic biomass (Kaur et al., 2020) and depends on the lignin content of the biomass (Rodriguez et al., 2017). The most common alkalis used in the pretreatment of lignocellulosic materials are sodium, ammonium, calcium and potassium hydroxides (Rodriguez et al., 2017; Sinbuathong et al., 2020). The alkali pretreatment was efficient to enhance the solubilization of organic matter and methane generation (Ali et al., 2020), and could enhance the degradation of cellulose, hemicellulose and lignin to 55.6%, 68.3% and 16.8% (Hu et al., 2016). In a previous study of alkali pretreatment using 6% NaOH (w/w), the methane potential was increased by 11.4% from raw DPEFB (Lahboubi et al., 2021b). They have reported that the combined alkali-thermal pretreatment has increased the methane potential by 21.52% from raw DPEFB. Besides, Salehian et al. (2013) had also studied the effect of NaOH on lignocellulosic material at two temperatures (0 and 100 °C) for different periods of time. They have found that 8% (w/w) NaOH was effective at 100 °C for 10 min with a 181.2% improvement of biogas production. On the other hand, even a high concentration of NaOH at low temperature decreases crystallinity by breaking the intramolecular hydrogen bonds between cellulose chains (Porro et al., 2007) and can dissolve the cellulose and regenerate it (Nieves et al., 2011), it can resulted in the decrease of methane production. Several experiments need to be conducted to reach the limit of using high alkali concentration in anaerobic digestion pretreatment. In a study of $Ca(OH)_2$ pretreatment of sugarcane bagasse (SCB) with concentrations of 1.7–11.9% of dry weight SCB for 4 h at room temperature, the methane potential of pretreated SCB 11.9% was lower than pretreated SCB 8.5% (Mustafa et al., 2018). The high concentration of NaOH can be reused on a large scale and in industry, which is very important from the perspective of the economy and environmental impact of the anaerobic digestion process (Nieves et al., 2011). To our knowledge, pretreatment with high alkali concentration using NaOH has not been really studied for the enhancement of biogas from DPEFB feedstock.

The kinetic study has become famous in bacterial growth. Modeling of microbial growth is used to estimate the specific growth rate and lag time (Ware and Power, 2017). It is practical to understand the ultimate methane production in a short time (Bakraoui et al., 2018; Habchi et al., 2022). Kinetic equations contained mathematical parameters, which have not biological meaning. Several authors have modified the mathematical parameters to biological meaning. The modified

Gompertz equation has become most commonly used for the prediction of methane production (Hernández-Fydrych et al., 2019).

The objective of this study is to evaluate the effect of high alkali pretreatment on date palm tree waste: empty fruit bunch, on methane production and biodegradability, and optimize the limit of the high alkali concentration. The alkali pretreatment used in this study is sodium hydroxide (NaOH), using three weight ratios: 6, 18 and 30% (w/w) (weight ratio of NaOH/weight of VS). The experiments are conducted using a CSTR digester with batch mode under mesophilic conditions. The kinetic study is applied to all experimental results to describe adequate fitting using the Modified Gompertz and the Transference function models. Anaerobic digestion of date palm trees has not been widely used in the literature, which is the strength of this study. This study was carried out in 2019–2020, at the Organic Chemistry Catalysis and Environment Laboratory, University Ibn Tofail, Kenitra, Morocco.

MATERIALS AND METHODS

Substrate preparation

The DPEFB substrate used in this study was collected from Valley ZiZ, Drâa region, which is located in the South of the Moroccan Atlas Mountains, Morocco. The substrate was ground using a blinder in order to minimize the size (size < 5 mm). The substrate was stored at 4 °C until use. This mechanical pretreatment was used as a control to find out the improvement of the proposed alkali pretreatment.

Alkali pretreatment was conducted using sodium hydroxide pellets EMPLURA (NaOH). 20 g of the substrate was treated with NaOH to prepare a ratio of 6, 18 and 30% (w/w) (ratio weight of NaOH/weight of VS). The prepared substrates were mixed with distilled water for 10 min under room temperature. The pretreated substrates were added directly to the digester to avoid having another effect on the substrate (Lahboubi et al. 2021b). The inoculum was provided from a full-scale digester of the vinasse industry in Kenitra City, Morocco, working under mesophilic conditions (37 °C). The bacteria used in this study are hydrolytic bacteria. The inoculum was stored at 4 °C until use. The physicochemical characterizations of inoculum, the raw and the pretreated substrate are shown in Table 1.

Anaerobic digestion set-up

The experimental batch set-up, shown in Figure 1, consists of a 5 L continuous stirred tank reactor (CSTR) digester (1), made of Pyrex, heated via a thermostatic jacket from a thermostat bath SELECTA model to ensure the mesophilic conditions (37±1 °C) (2). The reactor is equipped with three orifices, one of the substrate feeding (3), one for mechanical stirring (two blade with a velocity of 200 rpm, model OS20-Pro - DLAB) (4) and one for biogas outlet (5). A bubbler contained a sodium hydroxide solution (NaOH) (6N) was used for CO_2 removal (6), and it was connected between the reactor and the gasmeter. The volume of methane is measured when the water moves from the cylindrical gasmeter, made of Pyrex, to a graduated tube by the water displacement method (7). The methane volume produced was daily measured using the graduated tube under the ambient condition of the room (8).

Chemical analysis

The Total Solid (TS) and the Volatile Solid (VS) were determined according to standard methods (APHA 1989). The TS was determined by drying the sample at 105 °C for 24 hours. The ashes were determined by burning the dried sample at 550 °C for 2 hours. The VS was calculated by the difference between TS and ashes. The moisture was determined according to the standard method (APHA 1989).

Experimental protocol

For each experiment, the inoculum was added to the digester with a VS ratio of 2:1 (inoculum: substrate). The inoculum was firstly activated in mesophilic conditions (37 °C) for two days until the methane production of the inoculum stopped. After the preparation of the raw and pretreated substrate, they were added directly to the digester after the activation of the inoculum. During the experiments, the pH was measured to ensure the stability of the process. The experiment was run in triplicate.

The substrate pretreatments have direct effects on AD performances in terms of methane potential and process stability. The raw and pretreated substrates were tested to evaluate these effects.
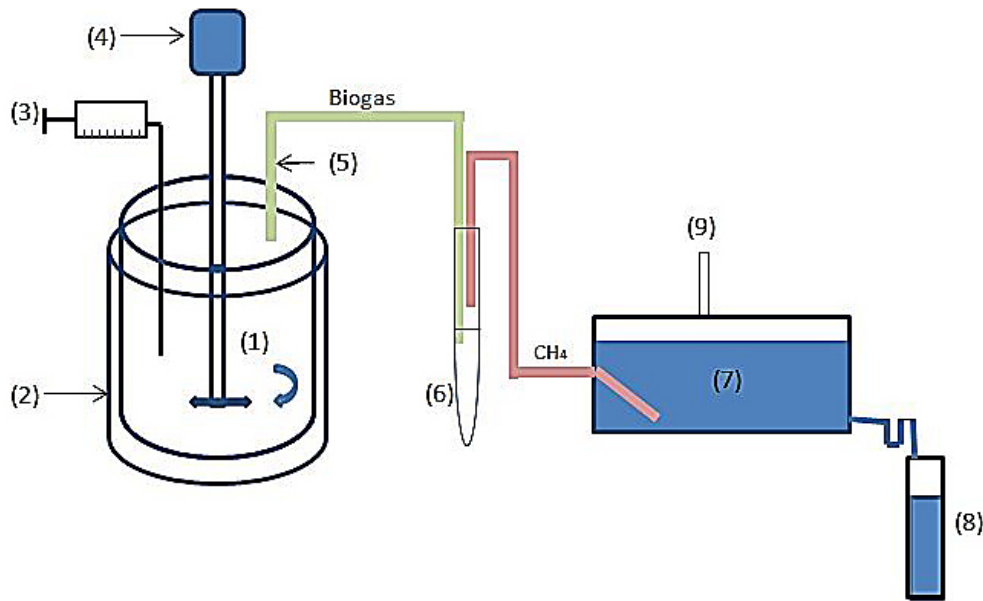
Figure 1. Scheme of the experimental batch set-up: (1) digester (dimension (L×W×H) 1300×440×460 mm), (2) thermostatic jacket, (3) substrate feed, (4) mechanical stirring, (5) biogas outlet, (6) sodium hydroxide solution, (7) gasmeter, (8) graduated tube, (9) methane outlet

The methane volume was standardized under ambient conditions (Lahboubi et al., 2020). The generated methane potential from DPEFB under experimental conditions was calculated per g of VS added (mL/gVS) as shown in Equation 1 (El Achkar et al., 2016):

$$PCH_4 \ (mL/gVS) = \frac{VCH4(mL)}{added \ VS(gVS)} \qquad (1)$$

Biodegradability

The biodegradability was determined by dividing the methane potential on the theoretical methane potential (TMP) of DPEFB (Buffiere et al., 2008; El Achkar et al., 2016) as shown in Equation 2. From a previous study of producing methane from DPEFB, the estimated TMP of DPEFB calculated using the Buswell equation was 405.3 mL/gVS (Lahboubi et al., 2020).

$$Bd \ (\%) = \frac{PCH4 \ (mL/gVS)}{TMP \ (mL/gVS)} * 100 \qquad (2)$$

Kinetic study

The curves of cumulative methane production can differ from one substrate to others. On one hand, the simple substrates, which were characterized by high biodegradability, had the reverse L-shape. On the other hand, complex substrates had the S-shape or stepped curve (Fig. 2) (Ware and Power, 2017).

In this study, two kinetic equations were applied: modified Gompertz and Transference function. Assuming that biogas or methane production depends on bacterial growth, the kinetic modeling was used to fit the experimental data (Rathaur et al., 2018). The theoretical data were obtained by adjusting the experimental methane production (N mL/gVS) for each experiment (El Gnaoui et al., 2020). The modified Gompertz and Transference function were described using Equations 3 and 4, respectively (Panigrahi et al., 2020):

Modified Gompertz:

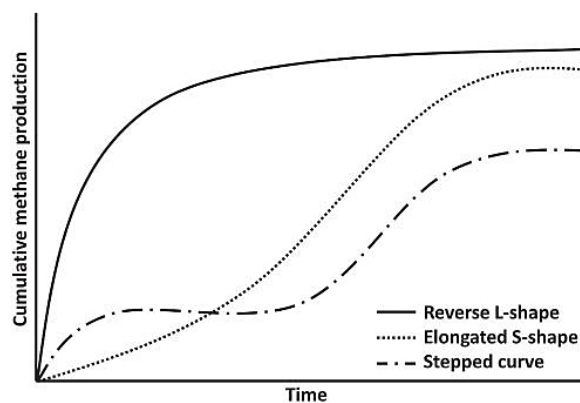$$P(t) = A * \exp(-\exp(\frac{\mu e}{A}(\lambda - t) + 1)) \qquad (3)$$

Figure 2. Typical cumulative methane production shapes (Ware and Power, 2017)

Transference function:

$$P(t) = A * \left[1 - \exp\left(\frac{\mu * (\lambda - t)}{A} \right) \right] \quad (4)$$

where: P – represents the simulated cumulative methane production (N mL/gVS), A – represents the simulated maximum cumulative methane production (N mL/gVS), μ – represents the methane production rate (N mL/gVS.d), λ – represents the lag phase time (d), and t – represents the digestion time (d).

RESULTS AND DISCUSSION

Substrate and inoculum characterization

The physicochemical characterizations of inoculum, raw and pretreated substrate are shown in Table 1. The pH of the inoculum is 8.03, which is considered as a suitable environment for anaerobic bacteria. As shown in Table 1, the raw and pretreated substrate had a high VS content. The results show that by increasing the amount of NaOH, the VS (%TS) content decreased from 83.89 to 68.10%, which can be explained by the fact that NaOH solubilizes the substrate VS (Heo et al., 2003). These VS can degrade with anaerobic bacteria to produce a significant amount of biogas, depending on the biodegradability of the substrate and process conditions. The hemicellulose, cellulose and lignin content of the raw substrate were 9.5, 16 and 9.4%, respectively (Lahboubi et al., 2020). The theoretical biogas and methane yield of the raw substrate are: 794 and 405 mL/gVS (Lahboubi et al., 2021a).

In research conducted by Dai et al., (2018), they reported that NaOH pretreatment decreased the percentages of hemicellulose and lignin in a lignocellulosic substrate (rice straw). They explained that the OH-band in NaOH can result the decomposition and separation of cellulose, hemicellulose and lignin by breaking the ester and ether bond between lignin and polysaccharides and weaken the hydrogen bonding between hemicellulose and cellulose (Dai et al., 2018). Salehian et al. (2013) had shown that alkali pretreatment using NaOH for 10 min retention time had decreased the lignin content of pine wood from 29.5 ± 0.2 to 27.9 ± 0.1%.

pH evolution

The stability of the process was evaluated through the pH. The pH must be followed up on a regular timeline to keep up the process monitoring. The optimum pH for AD stability was between 6.5 and 8.5, near neutrality. The Figure 3 shows the results of the pH of the raw and pretreated substrate throughout the experiment. During the experiment, the pH values were between 7.4–7.8 for the raw substrate, and 6.5–7.7 using the alkali pretreatment. The AD of the raw and the pretreated substrate was in pH conditions insuring the process stability. As shown in Figure 3, the pH values of the 30% (w/w) were between 6.3 and 7.7, with a mean value of 7.17. The decrease in pH, which appears after 40 days of methane production, was probably due to an inhibition problem due to the accumulation of acids with high content in NaOH. Besides, the pH decrease during the experiment was expressed by the production of acids causing the imbalance of the acidogenic and methanogenic phases of AD (Bakraoui et al., 2019). The same observation was observed by Al-Juhaimi et al. (2014), who concluded that the decrease in pH was due to the accumulation of the non-acetate fatty acids that are not directly metabolizable by methanogenic bacteria.

Table 1. Physicochemical characterization of inoculum, raw and pretreated substrate

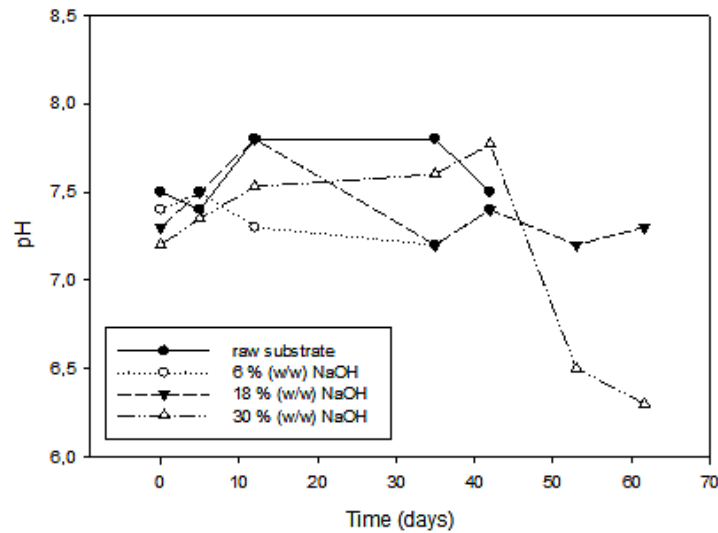| Parameters	Inoculum	Raw substrate	NaOH pretreatment (w/w)		
			6%	18%	30%
pH	8.03	-	8.6	10.6	13.2
TS (g/kg)	23.63	867.23	170.06	201.92	138.79
VS* (g/kg)	8.86	797.08	142.65	140.38	94.51
TS (%)	2.35	86.74	16.98	19.13	9.21
VS (%TS)	37.50	91.91	83.89	69.52	68.10

* Basis on dry sample.

Figure 3. pH evolution during mesophilic anaerobic digestion of raw and pretreated DPEFB

Methane potential

The AD results of the raw and the pretreated substrate are represented in Table 2 and Figure 4. The cumulative methane potential of the raw and the pretreated substrate had increased with time. The cumulative methane potential of the raw substrate was 98.5 N mL/gVS. The low methane potential might be due to the composite nature of the substrate with insoluble fraction lignin (Chandrasekhar et al., 2020). Moreover, the alkali pretreatment results showed that the 6 and 18% (w/w) NaOH had improved the methane potential from 98.5 NmL/gVS to 107 and 204 N mL/gVS (Fig. 4), respectively (with 8 and 104% of improvement), which showed the positive impact of the alkali pretreatment on the substrate. The concentration of 18% is considered high, but has a positive impact on methane potential and biodegradability. The high pretreatment with 30% (w/w) was not effective since the methane potential was lower than the untreated substrate (97 N mL/gVS). It is concluded that a higher concentration of NaOH was not effective for methane production improvement, which may lead to problems of inhibitions. The fail in improvement using alkali pretreatment was due to the limitation of the process pretreatment (Anu et al., 2020). Al-Juhaimi et al. (2014) had reported that the decrease in pH resulted in a decrease in biogas production. Kainthola et al. (2019), reported that even if the chemical pretreatment improved the biodegradation of the substrate, it may produce inhibitory compounds that have an effect on anaerobic digestion obstruction. In another study
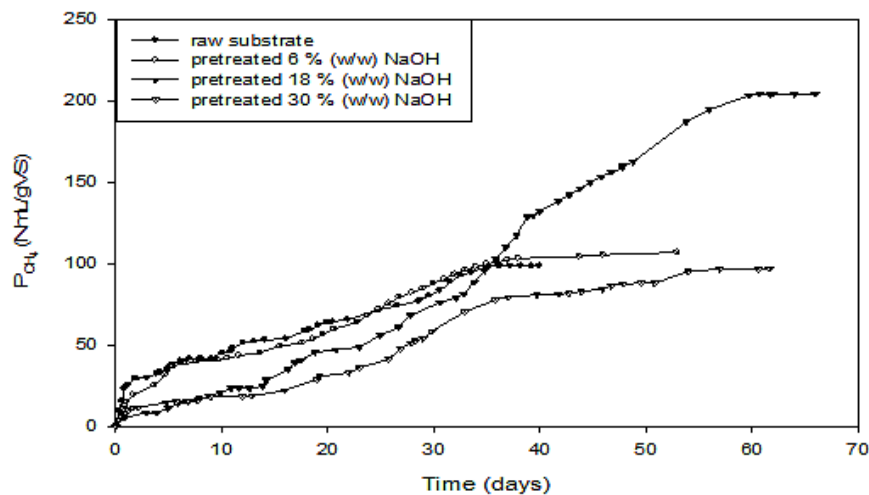

Figure 4. Cumulative methane production for raw and pretreated DPEFB

Table 2. The methane potential and methane improvement of lignocellulosic substrates

NaOH pretreatment (w/w)	Substrate	P_{CH4} (N mL/gVS)	Methane improvement (%)	Reference
Raw substrate	DPEFB	98.5	-	This study
6 %		107	8	
18 %		204	104	
30 %		97	-2	
6 %	EFB	132	11.4	(Lahboubi et al. 2021b)
8 %	Pine wood	-	181	(Salehian et al. 2013)
8 %	Oil palm empty fruit bunch	-	83	(Nieves et al. 2011)

of producing methane from an oil palm empty fruit bunch, alkali pretreatment was effective with an improvement of 83% after pretreatment with 8% (w/v) NaOH for 60 min (Nieves et al., 2011). In a study of alkali pretreatment of pine wood (a lignocellulosic substrate), the best improvement of methane production was achieved with 8% NaOH for 10 min at 100 °C, with an improvement of 181% of methane yield (Salehian et al. 2013). Yang et al. reported that with alkaline addition the hydrolytic bacteria were decreased (Yang et al., 2020).

Biodegradability

The results of biodegradability calculations are represented in Table 3. The biodegradability (Bd) was increased with increasing alkali load (respectively 26 and 50%) and higher than the biodegradability of the raw substrate (24%). Unlike for the last alkali load (30% NaOH), the biodegradability stayed the same as

Table 3. Experimental methane potential and biodegradability for the different experiments

Parameters	P_{CH4} (N mL/gVS)	Bd (%)
Raw substrate	98.5	24
NaOH pretreatment (w/w)		
6 %	107	26
18 %	204	50
30 %	97	24

the raw substrate (24%) (Fig. 5), which shows that the high pretreatment of 30% (w/w) was not effected too on increasing the biodegradability. The fail in biodegradability in the 30% (w/w) pretreatment may be caused by the inhibition problem with a high concentration of NaOH. From a previous study of producing methane from DPEFB, the theoretical biodegradability was 28.13% (Lahboubi et al, 2020). From these results, the pretreatment with low NaOH concentrations up to 18% improves the biodegradability.
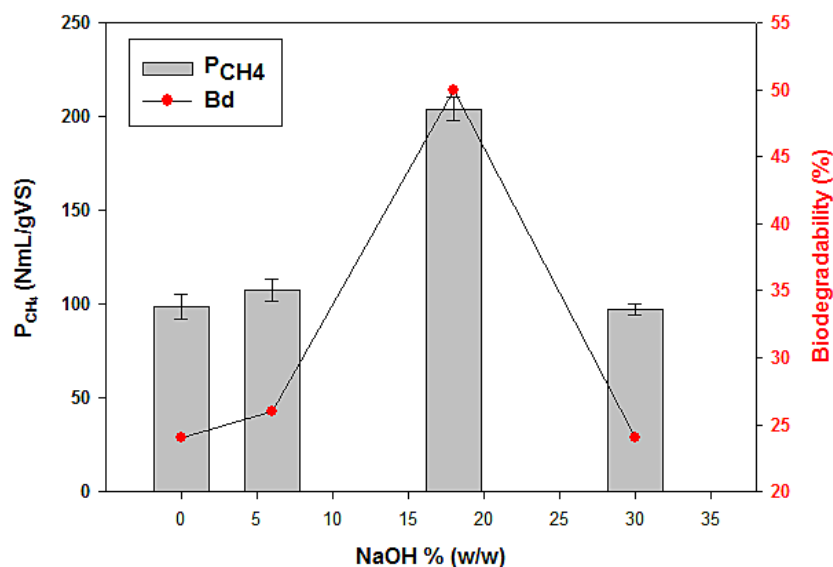

Figure 5. Methane potential and biodegradability as function of pretreated NaOH % (w/w)

Kinetic results

Table 4 represents the results of the kinetic study. The kinetic models used in this study had fitted well and allowed to determine the R^2, lag phase and the maximum methane production rate. Figure 6 represents the kinetic parameter curves.

The results show that the pretreatment with NaOH ratio 18% (w/w) had the best fitting in terms of R^2 and methane production rate. The methane production rate of the treated substrate (6 and 18%) was higher than the one of the untreated substrate, noticing that the transference methane production

Table 4. Kinetic parameters of modified Gompertz and transference function

| Parameters	Models	P_{CH4} (N mL/gVS)	A (N mL/gVS)	μ (N mL/ gVS.d)	λ (d)	R^2	Error (%)
Raw substrate	Modified Gompertz	98.5	99.1	2.35	0	0.9568	0.61
	Transference		98.62	2.39	0	0.9506	0.12
NaOH pretreatment (w/w)							
6 %	Modified Gompertz	107	112.8	2.79	0	0.9652	5.42
	Transference		110.23	2.88	0	0.9616	3
18 %	Modified Gompertz	204	210.9	4.4	11.7	0.944	3.4
	Transference		206.27	5	14.82	0.996	1.11
30 %	Modified Gompertz	97	100.8	2.17	3.75	0.9833	3.8
	Transference		96.73	2.5	6.9	0.9847	0.27
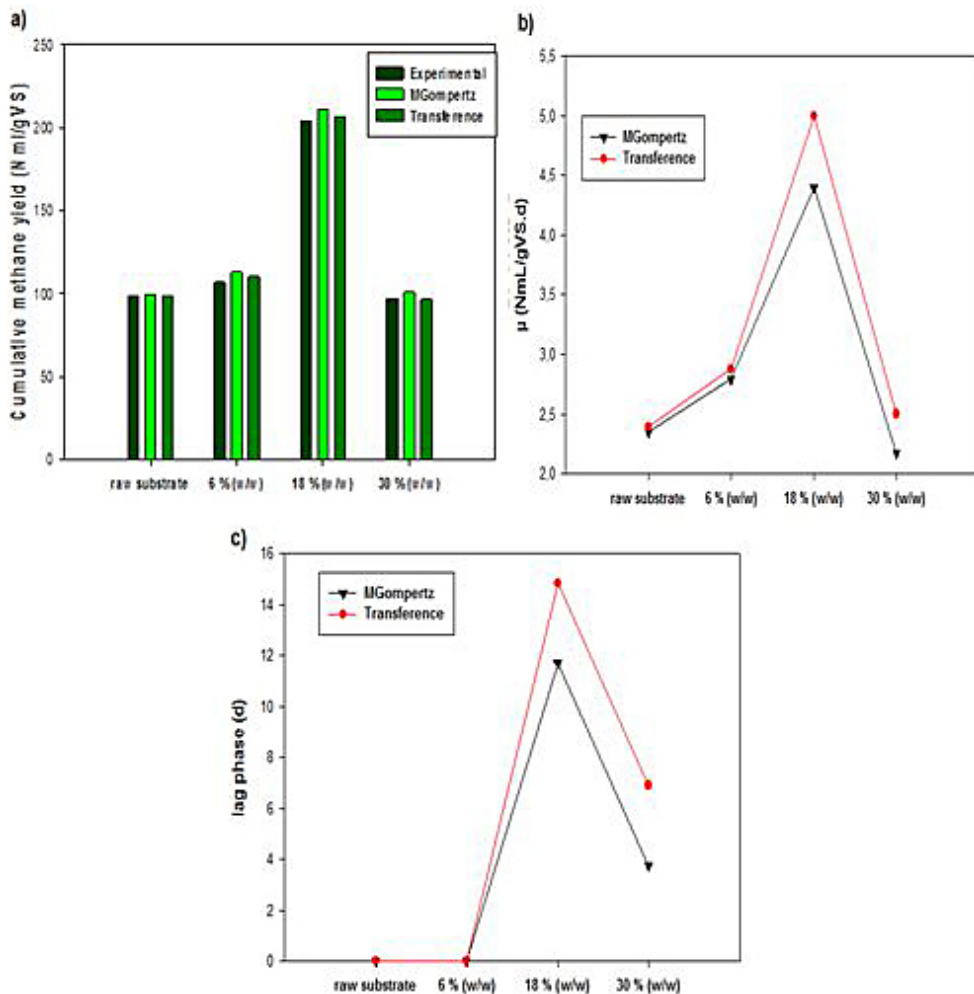
Fig. 6. Effect of alkali pretreatment on kinetics parameters for two models; (a) maximum cumulative methane production ; (b) methane production rate; (c) lag phase
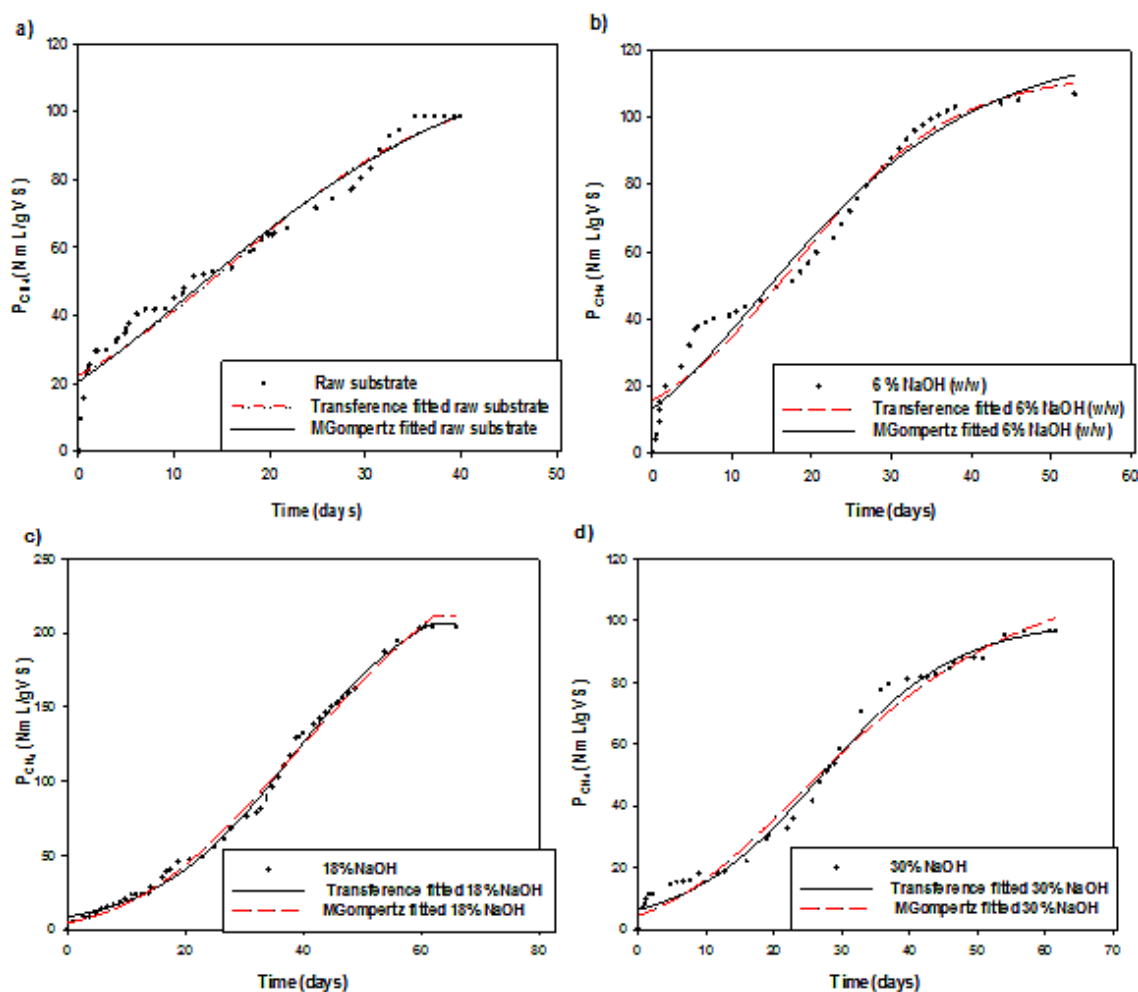
Fig. 7. Experimental cumulative and simulated methane production using Transference equation and MGompertz for: (a) raw substrate, (b) pretreated 6% (w/w) NaOH, (c) pretreated 18% (w/w) NaOH and (d) pretreated 30% (w/w) NaOH

rate was higher than the one of modified Gompertz. The same result was observed in another study, which showed that alkali pretreatment using NaOH improves the maximum methane production rate (Edwiges et al., 2019). The values of λ (lag phase) were ranged from 3.75 to 14.82 correspond to the pretreated 18 and 30% (w/w) and higher than the raw and pretreated 6% (w/w) which showed a higher concentrations of NaOH take more time for degradation. Mainardis et al., had shown that the high lag phase from the modified Gompertz could result from the significant lignin content in the substrate. The proposed pretreatment improves the methane production rate, but it is not effective in shortening the lag phase for instant degradation.

Figure 7 shows the curves of the experimental cumulative methane production and the kinetic curves. As shown in Figure 7, the curves of cumulative methane production for raw substrate and

pretreated NaOH ratio 6, 18 and 30% (w/w) have the stepped curve and elongated S-shape, which was defined by the nature and complexity of the substrate. The modified Gompertz and Transference functions were adjusted to experimental data. It can be concluded that the best fitting was in the pretreated NaOH ratio 18% (w/w) in terms of transference function. The errors between the experimental and fitted results were less than 10%, which can be notice that the fitted models can be applied to predict the methane potential. The same observation was concluded by Panigrahi et al. (2020) who obtained low error values less than 15%.

CONCLUSIONS

Date palm trees produce a large quantity of waste in Morocco that is poorly managed and lead to environmental problems. These wastes can be

biomass sources for producing renewable energy via the anaerobic digestion process. The date palm empty fruit bunch could not easily converted to biogas due to it lignocellulosic nature. For this reason, alkali-NaOH pretreatment is used to improve the methane potential and biodegradability. The best improvement (104%) was achieved with NaOH 18% (w/w), with a biodegradability of 50%. The results on data fitting showed that both models had better fits to experimental methane potential on pretreated 18% NaOH. The proposed pretreatment improves the methane potential, biodegradability and methane production rate. This study may provide useful information for the limitation of using high alkali pretreatment on DPEFB biomass. The result obtained in this study shows interesting information for producing methane as a clean energy production in the future.

Acknowledgements

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