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ANAEROBIC DIGESTION AND PRETREATMENT METHODS APPLIED TO PRIMARY AND SECONDARY SLUDGE FROM PULP AND PAPER MILLS: A REVIEW OF THE DEVELOPMENT OF GLOBAL RESEARCH AND A CASE STUDY OF A TYPICAL BRAZILIAN KRAFT PULP MILL

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Abstract: Pulp and paper (P&P) mills are currently one of the largest industrial water consumers and effluent generators worldwide. As a consequence of the biological effluent treatment processes currently in use, a large volume of sludge is generated, which requires great efforts and high costs to manage. An interesting option for sludge management is anaerobic digestion, a means of reducing sludge volume while generating renewable energy that can be used in the industrial processes. However, anaerobic technology needs to be improved, mainly due to the 30- to 40-d retention time required to digest pulp mill sludge in conventional anaerobic bioreactors. This paper presents a review of the potential of anaerobic digestion for sludge treatment in P&P mills and the application of pretreatment methods to enhance methane production, decrease the retention time and, ultimately, decrease the volume of the digesters. A case study examining the potential of integrating pretreatment and anaerobic sludge digestion in a Brazilian kraft pulp mill is also presented. The literature review resulted in 52 matches in which 16 articles were related to anaerobic digestion or co-digestion of P&P sludge without pretreatment and 20 articles had to do with anaerobic digestion of P&P sludge after pretreatment. A large discrepancy among the results presented made it difficult to assess the suitability of anaerobic digestion and the actual impacts of the sludge pretreatment on the viability of the system. Aspects such as the type of pulping process, sludge moisture and organic (original COD) content, as well as the pretreatment and the anaerobic testing conditions, seem to influence the methane yield. Simulations were carried out using current data from a Brazilian kraft pulp mill and indicated the important role of sludge pretreatment in potential methane production. Pretreated sludge has a theoretical potential to produce 4.7 times more methane than raw sludge, due the increase in the initial BOD as a result of the solubilization provided by the pretreatment.

Keywords: Anaerobic bioconversion; biogas; energy production; solid wastes

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INTRODUCTION

For centuries, pulp and paper (P&P) have been essential for human activities, including common uses such as packaging, hygiene, printing and writing, and also in the fabrication of innovative products based on carbon fibers.

A successful economic sector, the market value of P&P products globally was US$ 63.3 billion in 2019, with an estimated increase to approximately US$ 79.6 billion by 2024 (Tiseo, 2021). However, along with the economic success, the environmental aspects of P&P industries must be considered.

The P&P sector is one of the largest water consumers and effluent generators worldwide. Fresh water consumption has declined from about 200 m^3 per ton of dried pulp (ADT) in the 1960s to the current 25 m^3/ADT in modern bleached kraft pulp mills, although an average volume of effluent generated has been estimated at 60 m^3/ADT (Reeve & Silva, 2000; Karlsson, 2010).

A successful process widely applied for effluent treatment in P&P mills is primary clarification followed by an activated sludge process, which can effectively reduce suspended solids, organic content and the toxicity from the effluents. Activated sludge is the most widely used biological treatment process for P&P mill effluents, but it is one of the main energy consumers in an effluent treatment plant (ETP) (Hynninen, 2008). The treatment process generates a high organic load of primary (PS) and secondary (SS) sludge, which are usually incinerated or disposed of in landfills (Bayr *et al*., 2013; Kamali *et al*., 2016).

Environmental pollution problems related to landfilling with sludge include subsoil leachate and greenhouse gas emission (O'Brien *et al*., 2002). Additionally, landfills are becoming increasingly unattractive and more expensive due to stricter regulations, reduced availability of land and greater public awareness. In Brazilian P&P mills, landfilling is still the most common practice, and has some negative aspects, including the high costs (US$ 30-40 per ton of sludge) and increasingly restrictive legislation (Simão *et al*., 2018).

Currently, there is a growing demand for sustainable methods of sludge management and energy recovery. Studies of P&P mill sludge are mainly focused on the pyrolysis process for converting sludge into bio-oil and biochar products (Reckamp *et al*., 2014), co-liquefaction in hot-compressed water for bio-crude production (Zhang *et al*., 2011), pelletization (Nosek *et al*., 2017), co-combustion with coal for energy generation in boilers (Coimbra *et al*., 2015), hydrothermal carbonization for hydrochar production (Mäkelä *et al*., 2016) and anaerobic digestion for methane production (Kamali *et al*., 2016).

Based on the successful application in municipal treatment plants (e.g., Hanum *et al*., 2019; Lackey *et al*., 2015; Bolzonella *et al*., 2005), anaerobic digestion (AD) has become an interesting alternative for the management of sludge in P&P mills. Some benefits include sludge stabilization, sludge disinfection and energy recovery in the form of biogas (Park *et al*., 2012). In addition, the digestate produced has a high potential for land application, promoting nutrient recycling during agricultural use, and the resulting reduction of losses of organic matter (Gomez *et al*., 2005).

The composition of P&P mill sludge varies according to the pulping process employed, the raw material used, and the effluent treatment technique applied. However, it is characterized by the presence of complex polymers, such as lignocellulosic compounds (Manesh, 2012; Lopes *et al*., 2018), which makes the anaerobic process a challenge due to the difficulty of achieving natural hydrolysis (Elliot & Mahmood, 2007). Pretreatment technologies have been studied in order to maximize the soluble fraction of the organic matter in sludge prior to applying anaerobic digestion, with promising results related to the increase of biogas production, removal of organic matter and reduction of the retention time required for anaerobic digestion (Meyer & Edwards, 2014).

This paper presents a review of existing literature concerning the potential of anaerobic digestion for sludge treatment in P&P mills and the application of pretreatment methods to enhance methane production. The effects of different pretreatment methods are analyzed in terms of solubilization of organic matter, biogas production, energy and economic aspects. The potential of the integration of pretreatment with anaerobic sludge digestion in a Brazilian P&P mill is also presented in a case study of a typical Brazilian *Eucalyptus* kraft pulp mill.

MATERIAL AND METHODS

Literature search ad analysis

The review method was carried out based on the eight-step proposal of Okoli & Schabram (2010). To determine the review's purpose, two guiding questions was asked, as follows: Is pulp and paper sludge suitable for anaerobic digestion? How can the methane yield be enhanced by applying pretreatment techniques in pulp and paper mills? Multiple keywords were determined for the search: anaerobic digestion, pulp, paper, sludge, biosludge, biochemical methane potential (BMP) assay, methane, pretreatment and hydrolyze.

The inclusion/exclusion criteria were established according to the following requirements: i) present research results; ii) explicit answers to the guiding questions in the title or abstract; and iii) treatment of the subject from a technical point of view.

The literature search process was carried out with the application of the search keywords in four peer-reviewed databases: ScienceDirect, SCOPUS, SciELO and Springer. All the results published until December 2020 were collected. Notes, theses, books or papers of an exclusively theoretical nature were excluded, as well as editorials.

The selected papers were divided into two groups, according to the presence or absence of pretreatment tests for enhancing anaerobic digestion. The operational conditions applied, and the resulting methane yield, are following discussed.

A case study of anaerobic digestion in a typical Brazilian kraft pulp mill

In order to evaluate the potential of anaerobic digestion, a simulation was performed using current data from a *Eucalyptus* bleached kraft pulp mill located in southeastern Brazil. The simulation included two conditions: the first using raw sludge without pretreatment, and the second with sludge previously solubilized by thermal pretreatment.

The selected mill produces approximately 1 million ADT/year. The mill effluent treatment plant consists of primary clarifiers followed by a conventional activated sludge secondary treatment. Secondary sludge samples were collected from the return line of the secondary clarifier and stored according to the sampling and sample preservation methods of the US Environmental Protection Agency (USEPA, 2013).

To simulate pretreated sludge, thermal hydrolysis was performed at 175 °C for 30 minutes. The tests were carried out in a 20-L pressurized Parr 4848 M Reactor (Parr Instrument Company, Moline, USA), with an internal mixer (200±10 rpm) and thermometer. For each pretreatment test, 4 L of secondary sludge were used. After loading the sludge sample, the headspace of the reactor was flushed with nitrogen gas to exclude oxygen and prevent any oxidation of the organic compounds. The heating rate was regulated at 9.5 °C per minute until reaching the maximum of 175 °C.

The sludge was characterized before and after the pretreatment tests for total chemical oxygen demand (tCOD) and soluble chemical oxygen demand (sCOD), according to standard method 5220-D (APHA, AWWA, WPC, 2012), and for biochemical oxygen demand (BOD_5) and ultimate biochemical oxygen demand (BODu), according to standard method 5210 (APHA, AWWA, WPC, 2012).

A single-stage high-rate anaerobic digester operating under mesophilic conditions at 35 °C was simulated according to Metcalf & Eddy (2013). The process design method applied was based on solids retention time (SRT), where the volume of methane produced was estimated from the sludge flow rate, the BODu influent and effluent, the conversion factor of methane from the BODu and the net mass of cell tissue produced per day. Following this and considering a complete-mix high-rate digester without recycling, the net mass of cells produced was calculated from the BODu influent and effluent, yield coefficient, endogenous coefficient and SRT.

The data used considered the theoretical conversion factor of methane produced from the conversion of 1 kg of BODu at 35 °C to be 0.40, the yield coefficient to be 0.08 mg SSV/mg BODu, the endogenous coefficient to be 0.03 d^{-1} and the efficiency of waste utilization to be 70%.

Aiming for a more complete understanding of the effects of pretreatment on sludge digestion, different scenarios related to the sludge flow rate and SRT were considered. For the sludge flow rate, simulations of 50%, 75% and 100% of the total exceeding sludge treated via anaerobic digestion were performed, corresponding to 1680 m^3/d, 2520 m^3/d and 3360 m^3/d, respectively; these values were calculated based on data from the mill collected over a 2-y period. For SRT, seven different values were simulated, ranging from 8 to 20 d, since, in practice for high-rate digestion, those SRT values are the most applied (Metcalf & Eddy, 2013).

RESULTS AND DISCUSSIONS

Global research on anaerobic digestion of sludge from pulp and paper mills

The search resulted in 104 matches, classified as follows: 58 research articles, 11 review articles, 5 encyclopedia articles, 8 book chapters, 16 conference abstracts, 1 short communication and 5 classified as “other”.

Some of the matches were excluded because they did not focus on pulp and paper sludge, but on municipal sewage sludge, food waste or other topics. Excluding these results, 53 matches remained, classified as follow:

i. 10 review articles (Rintala & Puhakka, 1994; Mahmood & Elliott, 2006; Elliott & Mahmood, 2007; Meyer & Edwards, 2014; Pontual *et al.*, 2015; Gottumukkala *et al.*, 2016; Kamali *et al.*, 2016; Veluchamy & Kalamdhad, 2017a; Chakraborty *et al.*, 2019; Grosser & Celary, 2019);

ii. 5 dissertations or theses (Karlsson, 2010; Hagelqvist, 2013b; Bayr, 2014; Huang, 2015; Lopes, 2017);

iii. 16 research articles about anaerobic digestion or co-digestion of P&P sludge without pretreatment (Boman & Bergström, 1985; Puhakka *et al*., 1988; Puhakka *et al*., 1992; Jokela *et al*., 1997; Lin *et al*., 2011; Bayr & Rintala, 2012; Parameswaran & Rittmann, 2012; Lin *et al*., 2013; Hagelqvist, 2013a; Huiliñir *et al*., 2014; Ekstrand *et al*., 2016; Hagelqvist & Granström, 2016; Veluchamy & Kalamdhad, 2017b; Chatterjee *et al*., 2018; Kokko *et al*., 2018; Lopes *et al*., 2018);

iv. 20 research articles about anaerobic digestion of P&P sludge with pretreatment (Lin *et al*., 2009; Wood *et al*., 2009; Wood *et al*., 2010; Lin *et al*., 2010; Karlsson *et al*., 2011; Saha *et al*., 2011; Mehdizadeh *et al*., 2012; Park *et al*., 2012; Elliott & Mahmood, 2012; Bayr *et al*., 2013; Tyagi *et al*., 2014; Kinnunen *et al*., 2015; Zhang *et al*., 2016; Lin *et al*., 2017; Veluchamy *et al*., 2017; Kolbl *et al*., 2017; Bonilla *et al*., 2018; Sethupathy & Sivashanmugam, 2018; Veluchamy *et al*., 2018; Sethupathy *et al*., 2020); and

v. 2 classified as "other" (Stoica *et al*., 2009; Priadi *et al*., 2013).

The effects of the anaerobic digestion tests with raw and pretreated P&P mill sludge which are mentioned in these sources are discussed in the following sections of this article.

Anaerobic digestion and co-digestion of P&P mill sludge without pretreatment

Research on anaerobic digestion and co-digestion of P&P mill solid residues started to be published in the 1980s and has demonstrated the potential of this technology. Promising results were shown, such as a reduction of 74% in the volatile solids (VS) content for mixed sludge from a kraft mill (Boman & Bergström, 1985) and a reduction of 36-41% of VS for mixed sludge from a thermo-mechanical pulp mill (Puhakka *et al*., 1988).

Although the research was initially promising, the results for the anaerobic digestion of P&P sludge without pretreatment showed a substantial variance in the methane yield (**Table 1**). For primary sludge (PS), the methane yield varied from 3.5 mL/gVS after batch assays for 30 d (Lopes *et al*., 2018) to 190-240 mL/gVS (Bayr & Rintala, 2012), both tested under thermophilic conditions. Lopes *et al*. (2018) explained that the low methane production was due to the lignocellulosic composition that confers low biodegradability to the pulp sludge and the accumulation of acetic acid during AD. Bayr & Rintala (2012) achieved more interesting results with the operation of a continuously stirred tank reactor (CSTRs) for 122 d of testing different hydraulic retention time (HRT) and organic loading rates (OLR).

The results regarding secondary sludge (SS) also varied greatly: 46.9 $mLCH_4/gVS$ in batch assays for 30 d (Lopes *et al*., 2018), 53 $mLCH_4/gVS$ in batch assays for 19 d (Hagelqvist, 2013a) and 220 mL/gVS in a CSTR operated during 21 months with varying OLR and HRT (Puhakka *et al*., 1992). However, the results achieved by these last authors represent the total biogas production and not that of methane alone, so no direct comparison can be made.

Mixed PS and SS has the lowest values of methane production reported, with 3.3 $mLCH_4/gVS$ in thermophilic batch assays for 30 d (Lopes *et al*., 2018). In contrast, Ekstrand *et al.* (2016) found a methane yield of 230 $mLCH_4/gVS$ with a high-rate CSTR under mesophilic conditions run for 800 d with the addition of Mg, K and S.

Lakes were used to discharge P&P mill wastewater before the implementation of wastewater treatment processes. For example, the bay area near an old pulp mill at Hiedanranta, in Tampere, Finland, received

Table 1. Results for anaerobic digestion and co-digestion of pulp and paper mill sludge

Methane yield ($mLCH_4/gVS$)					
Primary sludge	Secondary sludge	Mixed sludge	Co-digestion	Lake sedimented fiber	Reference
-	-	50-90	-	-	Puhakka *et al*., 1988
-	220[(1)]	-	-	-	Puhakka *et al*., 1992
-	-	-	180	-	Jokela et al., 1997
-	-	-	200	-	Lin et al., 2011
190-240	-	150-170	-	-	Bayr and Rintala, 2012
-	-	-	0.25[(2)]	-	Parameswaran and Rittmann, 2012
-	-	-	80	-	Hagelqvist, 2013a
-	-	-	432	-	Lin et al., 2013
-	-	-	183	-	Huilinir et al., 2014
-	-	230	-	-	Ekstrand et al., 2016
-	-	-	50	-	Hagelqvista and Granström, 2016
3.5	46.9	3.3	-	-	Lopes et al., 2018
-	-	-	-	250	Kokko et al., 2018
-	-	-	-	201	Chatterjee et al., 2018

[(1)] results for total biogas (not only methane)
[(2)] $LCH_4/Lreactor.d$

effluents from a sulfite pulp mill from the 1910s to the 1980s, and has been estimated to contain about 1.5 million m³ of sedimented fibers that form a layer up to 10 m thick (Kokko *et al*., 2018). The potential for anaerobic digestion of the sedimented fiber from this lake was studied by Kokko *et al*. (2018) in batch assays, and by Chatterjee *et al*. (2018) in CSTR, with similar results for methane yield of 250 mLCH_4/gVS and 201 mLCH_4/gVS, respectively.

Co-digestion seems to be the best option for improving methane yield when pretreatment methods are not applied. The tested conditions included the mixture of P&P sludges (primary and secondary) with municipal sewage sludge (Jokela *et al*., 1997; Hagelqvist, 2013a), monosodium glutamate waste liquor (Lin *et al*., 2011), pig waste (Parameswaran & Rittmann, 2012), food waste (Lin *et al*., 2013), natural zeolite as catalyst (Huilinir *et al*., 2014) and pig and dairy manure (Hagelqvista & Granström, 2016). The best results were achieved by Lin *et al*. (2013), with a methane yield of 432 mLCH_4/gVS using a mixture of pulp and paper sludge and food waste with a 1:1 VS ratio as the feedstock in a two-stage anaerobic process (72-82 d of hydrogen fermentation followed by 28 d of methane fermentation). Despite the excellent results on the laboratory scale, the strategy used by Lin *et al*. (2013) demands a more robust anaerobic digestion plant with two anaerobic reactors and a high operational control for an acidification phase in the first reactor and a methanogenic phase in the second reactor.

Despite some promising results, the high cost of implementation, operation and maintenance have been cited as the main reason for the lack of full-scale anaerobic digesters in P&P mills (Meyer & Edwards, 2014). The main challenge is the difficulty of hydrolyzing lignocellulosic compounds, which results in the need for a high HRT (30 d) to achieve adequate digestion. Also, there is a lack of economic studies, since none of the research papers cited considered this aspect. In this scenario, it is clear that the AD process of raw PS and SS sludge requires improvements to compete with other technologies in P&P industries.

Anaerobic digestion of P&P mill sludge with pretreatment

Currently, pretreatment methods are being studied to make the AD of P&P mill sludge feasible. Several methods have already been proposed, based on biological, chemical, thermal, electrical and mechanical processes, with promising results for increasing biogas production, the removal of organic matter and the reduction of the required HRT (Elliott & Mahmood, 2007; Meyer & Edwards, 2014; Kamali *et al*., 2016). The main objective of pretreating sludge is to promote improvements in the hydrolysis of polymeric organic matter, which is considered the limiting step for the AD process. The benefits associated with the solubilization of sludge prior to anaerobic process are twofold: first, the increase in the amount of soluble substrate significantly increases the generation of organic acids for subsequent biogas production; and second, pretreatment decreases the viscosity of the sludge, which permits a higher concentration of solids (Elliott & Mahmood, 2007). Another important benefit of sludge pretreatment is the increase in the production rate of methane, reaching more than 70% of total biogas generation within the initial 10 d (Tyagi *et al*., 2014). **Table 2** summarizes the main results related with the application of pretreatment to P&P mill sludge.

High-intensity ultrasound devices are commonly used to generate high frequency waves. For P&P mill sludge, the most frequent is the use of 20 kHz, with retention time varying from 15 to 90 min (Wood *et al*., 2009; Saha *et al*., 2011; Elliott & Mahmood, 2012; Mehdizadeh *et al*., 2012). Operational parameters include initial COD ranging from 12 g/L (Wood *et al*., 2009) to 40 g/L (Saha *et al*., 2011; Elliot & Mahmood, 2012) and COD solubilization ranging from 0% to more than 400% (Wood *et al*., 2009). There is also a great variation in the resulting methane yield, varying from cases where no increase is observed when compared to raw sludge (Wood *et al*., 2009; Karlsson *et al*., 2011) to other cases where there is an increase of more than 140% (Saha *et al*., 2011; Mehdizadeh *et al*., 2012; Tyagi *et al*., 2014).

For the microwave method, the most common frequency is 2450 MHz, with temperature varying from 50 °C to 175 °C (Saha *et al*., 2011; Mehdizadeh *et al*., 2012). Initial COD, between 21 g/L (Tyagi *et al*., 2014) and 40 g/L (Saha *et al*., 2011), showed an increase in solubilization of more than 130% (Tyagi *et al*., 2014). Unlike ultrasound pretreatment, microwave resulted in an increase in methane yield when compared to raw sludge in all the studies consulted (Saha *et al*., 2011; Mehdizadeh *et al*., 2012; Tyagi *et al*., 2014).

Thermal hydrolysis of P&P mill sludge has already been tested for temperatures between 70 °C (Bayr *et al*., 2013) and 200 °C (Zhang *et al*., 2016), with retention times between 10 min (Bayr *et al*., 2013) and 120 min (Kinnunen *et al*., 2015). Longer retention time conditions are generally related to lower temperatures. Initial soluble COD of 1.4 g/L for SS from a sulfite mill and 0.3 g/L for SS from a kraft mill, increased 607% and 2167%, respectively, after thermal pretreatment (Wood *et al*., 2009). Methane yields increased more than 300% for SS from a kraft mill under mesophilic digestion conditions (Wood *et al*., 2009) and 100% for SS from a kraft mill using thermophilic digestion (Bayr *et al*., 2013).

Table 2. Main studies concerning pretreatment techniques for p&p sludge solubilization prior to anaerobic digestion, and their results.

Methane yield [1] $mLCH_4/gVS$; [2]$mLCH_4/gCOD$; [3]mL						References
Ultrasound	**Microwave**	**Thermal**	**Alkaline**	**Biological**	**Mechanical / electrical**	
55-200[2]	-	180-300[2]	-	-	-	Wood *et al.*, 2009; 2010
-	-	-	260-320[1]	-	-	Lin *et al.*, 2009
-	-	-	-	170-230[1]	-	Lin *et al.*, 2010
158-209[1]	-	-	-	240[1]	-	Karlsson *et al.*, 2011
95-120[2]	89-130[2]	-	-	-	100[2]	Saha *et al.*, 2011
20-90[2]	-	-	-	-	40-100[2]	Elliot & Mahmood, 2012
80-131[2]	94-136[2]	-	-	-	-	Mehdizadeh *et al.*, 2012
114[1]	-	112-134[1]	86[1]	114[1]	-	Bayr *et al.*, 2013
5175[3]	4895[3]	-	-	-	-	Tyagi *et al.*, 2014
-	-	60-124[1]	-	-	-	Kinnunen *et al.*, 2015
-	-	100-182[1]	-	-	-	Zhang *et al.*, 2016
-	-	-	-	429[1]	-	Lin *et al.*, 2017
-	-	-	-	147-195[1]	-	Kolbl *et al.*, 2017
-	-	-	-	50-175[1]	-	Sethupathy & Sivashanmugam, 2018
	-	-	-	140-220[2]	-	Bonilla *et al.*, 2018
	-	-	-	-	301[1]	Veluchamy *et al.*, 2017; 2018
	-	-	-	295[1]		Sethupathy *et al.*, 2020

Thermal hydrolysis also resulted in an important improvement in the rate of methane production. Wood *et al.* (2009) generated approximately 220 $mLCH_4/gCOD$ after 15 d, 250 $mLCH_4/gCOD$ after 20 d and 300 $mLCH_4/gCOD$ after 30 d for SS from a sulfite mill using thermal pretreatment, showing that more than 70% of the total methane was generated during the first 15 d. The methane yield of the raw sludge was approximately 100 $mLCH_4/gCOD$ after 15 d, 125 $mLCH_4/gCOD$ after 20 d and 200 $mLCH_4/gCOD$ after 30 d, significantly lower than the pretreated sludge.

Considering the chemical methods for sludge pretreatment, the most common is the addition of alkali (NaOH) until pH 12 is reached. However, for successful sludge solubilization, a long retention time is required, more than 6 h (Lin *et al.*, 2009). Bayr *et al.* (2013) did not find an increase in the methane yield after alkaline pretreatment at pH 12 for 24 h. In contrast, Lin *et al.* (2009) found an increase of 150-184% after alkaline pretreatment, but the authors used a mixture of PS and SS with monosodium glutamate waste liquor in order to get an optimal C/N ratio, which could be the reason for the improvement in the methane yield.

Acid pretreatment (HNO_3 at pH 3) was also tested, but no improvement was observed because of the inhibition of hydrolysis and methane production, as demonstrated by the long lag phase (25 d) and the low methane production rates (Bayr *et al.*, 2013).

With the combination of thermal and alkaline sludge pretreatment strategies (140 °C, pH 12 for 60 min), Wood *et al.* (2009) found an increase in the methane yield of 115% and 340% for SS from a sulfite mill and a kraft mill, respectively. These results are lower than those achieved by the same authors with only thermal pretreatment, where an increase of 150-360% in methane yield was reached.

Biological pretreatment involves the use of hydrolytic enzymes, such as the mixture of cellulases, proteases and lipases (Karlsson *et al.*, 2011), accelerases, proteases, glycosidades and lysozymes (Bonilla *et al.*, 2018), mushroom compost (*Pleurotus ostreatus*) (Lin *et al.*, 2010), a microbial consortium (Lin et al., 2017) and biosurfactant (Sethupathy *et al.*, 2020). Methane yield after biological treatment varied from 50 $mLCH_4/gVS$ (Sethupathy & Sivashanmugam, 2018) to 429 $mLCH_4/gVS$ (Lin *et al.*, 2017); however, the highest value was observed for co-digestion of SS, rice straw and monosodium glutamate waste liquor, which may be the reason for the increment in the methane yield which this technique produced (Lin *et al.*, 2017).

Regarding the methane production rate, Karlsson *et al.* (2011) found a production of 70% of the total biogas during the first 20 d after enzyme pretreatment. In contrast, Bayr *et al.* (2013) did not find any improvement in the methane production rate when using a biological pretreatment. Difficulties related with enzyme selection, enzyme preparation and sludge characteristics seem to affect sludge digestibility, making the results discrepant between the different studies.

For mechanical pretreatment methods, beside microwave and ultrasound, Microsludge® seems to be a promising technology that combines chemical and mechanical disintegration for a more complete and rapid solubilization. The effects of Microsludge® were demonstrated in two publications. First, Saha *et al.* (2011) found a methane yield of 100 $mLCH_4/gCOD$, 125% higher than the control. In the second publication evaluated, Elliot & Mahhmood (2012) found an increase in methane yield from 12-77 $mLCH_4/gCOD$ (raw sludge) to 71-99 $mLCH_4/gCOD$ (pretreated with Microslude®), with results varying according to operating conditions.

More recently, an electrical method was tested, which is described as the most effective strategy for pulp and paper mill sludge hydrolysis (Veluchamy *et al*., 2017). Electrohydrolysis was tested by Veluchamy *et al*. (2017, 2018), achieving a high methane yield of 301 $mLCH_4/gVS$, versus 274 $mLCH_4/gVS$ for raw sludge. The authors explained that electrohydrolysis pretreatment followed by an anaerobic digestion process is a simple and sustainable strategy for waste stabilization and utilization in P&P mills, even though the energy consumed in the pretreatment seems higher. However, no detailed information about energy consumption and economic issues was presented.

The following hybrid strategies were also studied: ultrasound plus thermal, ultrasound plus biological, ultrasound plus thermal and biological (Bayr *et al*., 2013), ultrasound plus alkaline (Park *et al*., 2012; Tyagi *et al*., 2014) and microwave plus alkaline (Tyagi *et al*., 2014). Tyagi *et al*. (2014) achieved the highest COD solubilization (76-78%) using combined microwave (175 °C) and alkaline (pH 12) pretreatment. Bayr *et al*. (2013) produced the highest methane yield (141 $mLCH_4/gSV$) with the combined ultrasound and thermal methods, but when they used only thermal pretreatment (150 °C for 10 minutes), the results were similar (134 $mLCH_4/gSV$).

Analyzing the present data, some of the pretreatment techniques showed great disadvantages. Biological pretreatment required great efforts for enzyme preparation and operational control, plus the additional cost related to the large amount of enzyme required. Ultrasound and microwave techniques, although appearing to be promising due to the increase in biogas yield, may not be advantageous due to the high costs associated with the installation and maintenance of these technologies. Park *et al*. (2012) estimated the application of ultrasonic pretreatment at US$ 21/m³, and US$ 22-27/m³ when alkali was added, emphasizing that even if the biogas were sold at a high price (US$ 10/GJ), the profit would only be US$ 1.4/m³, without considering the costs of installation and maintenance. For Saha *et al*. (2011), under all the tested conditions for microwave (50-75 °C, 2450 MHz) and for ultrasonic waves with more than 15 min of retention time (frequency of 20 kHz), a negative energy balance was verified, which indicates that the cost with the pretreatment is higher than the possible profit related to the generation of biogas.

Thermal and alkaline pretreatment resulted in an increase in COD solubilization and in methane yield (Wood *et al*., 2009; Lin *et al*., 2009). These options seem to be the simplest for full-scale implementation, since they can benefit from the mill's own resources. Sources of alkalinity are common, due to the materials used in the pulping process, mainly in chemical pulp mills (both sulfite and kraft processes). Also, heat energy, commonly in the form of high-pressure steam generated in the recovery boiler, can be used as the heat source for the pretreatment and anaerobic reactors, thus reducing the operating costs.

The large discrepancy among the results presented does not allow us to assess the real impacts of pretreatment. Aspects such as the type of pulping process, sludge moisture and organic (original COD) content seem to influence the methane yield results, together with the pretreatment conditions. The need for further studies in order to optimize the operating conditions and clarify the real impacts of pretreatment on sludge solubilization is clear.

A case study of anaerobic digestion of secondary sludge in a typical Brazilian kraft pulp mill

Simulations were performed in order to evaluate the potential of anaerobic digestion in a typical Brazilian kraft pulp mill, since the data in the literature consulted did not allow us to evaluate the suitability of anaerobic digestion and the real impacts of pretreatment. The scenarios evaluated included: 50% (1680 m³/d), 75% (2520 m³/d) and 100% (3360 m³/d) of the total exceeding sludge treated with anaerobic digestion and SRT varying from 8 to 20 d.

Table 3 shows the results for sludge characterization performed before and after the pretreatment tests. Pretreatment solubilized the secondary sludge considerably, since all the evaluated parameters increased after the tests. Comparing pretreated sludge with raw sludge, tCOD increased 143%, sCOD increased 965%, BDO_5 increased 485% and BODu increased 469%. For the anaerobic digestion simulation, this provides a more soluble form of organic matter entering the digesters, resulting in a higher potential for methane production. Similar results are reported by Wood *et al*. (2009) and Bayr *et al*. (2013), both with an increase in soluble organic matter after thermal pretreatment of P&P mill sludge that resulted in an increase in the methane yield after batch assays.

Table 3. Characterization of organic matter from secondary sludge, performed before and after thermal pretreatment tests

Parameters	Raw sludge	Pretreated sludge
tCOD (mg/L)	7549±173	10,823±552
sCOD (mg/L)	1112±22	10,729±492
BOD_5 (mg/L)	570±34	2765±36
BODu (mg/L)	856±97	4015±235

Figs. 1−3 represent the results obtained in the simulations of anaerobic digestion. It is important to observe a major impact of SRT on the volume of the digesters. Considering the simulated case where 100% of the total exceeding sludge was treated using anaerobic digestion, the necessary digester volume increased 2.5 times, from 26880 m³ (SRT of 8 d) to 67200 m³ (SRT of 20 d). Considering the methane production estimated in this scenario, the increase was not so significant: from 2912 m^3CH_4/d (SRT of 8 d) to 3107 m^3CH_4/d (SRT of 20 d), an increase of only 1.07 times.

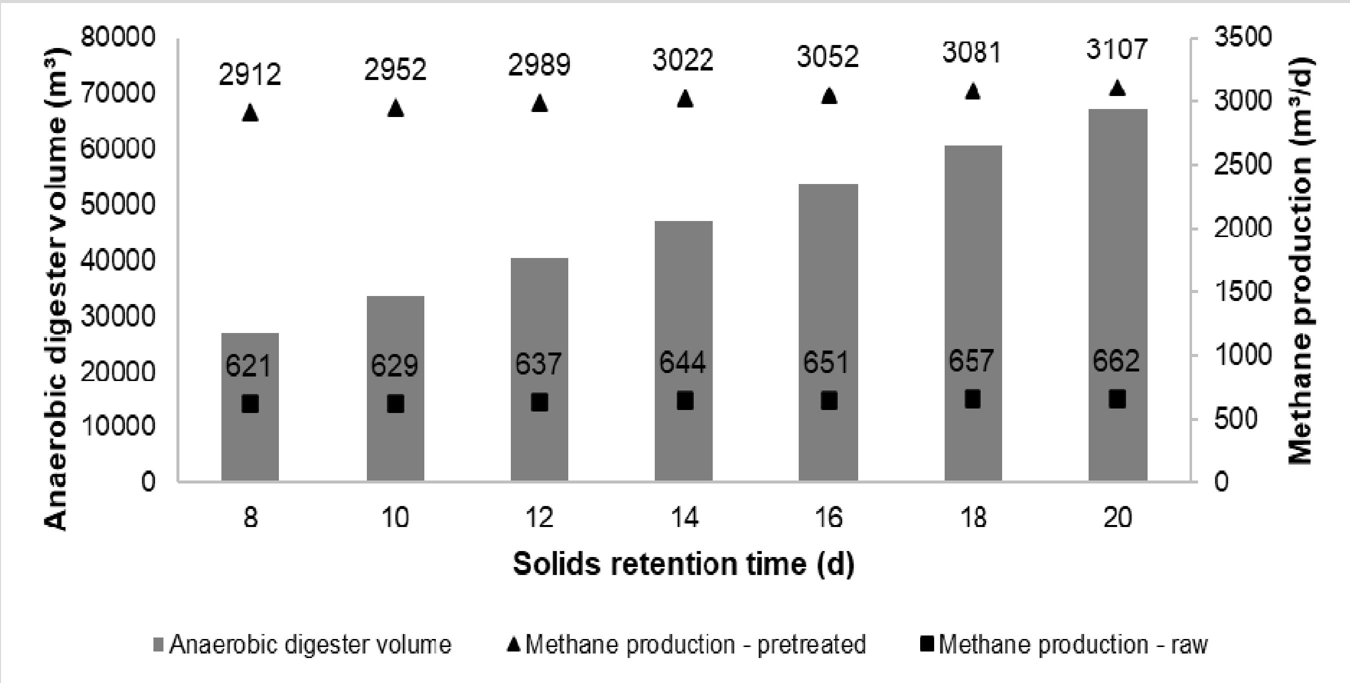

Fig. 1 Simulation of the anaerobic digestion process in a typical Brazilian bleached *Eucalyptus* kraft pulp mill, using raw and pretreated secondary sludge as substrate and considering 100% of the total exceeding sludge treated with anaerobic digestion.

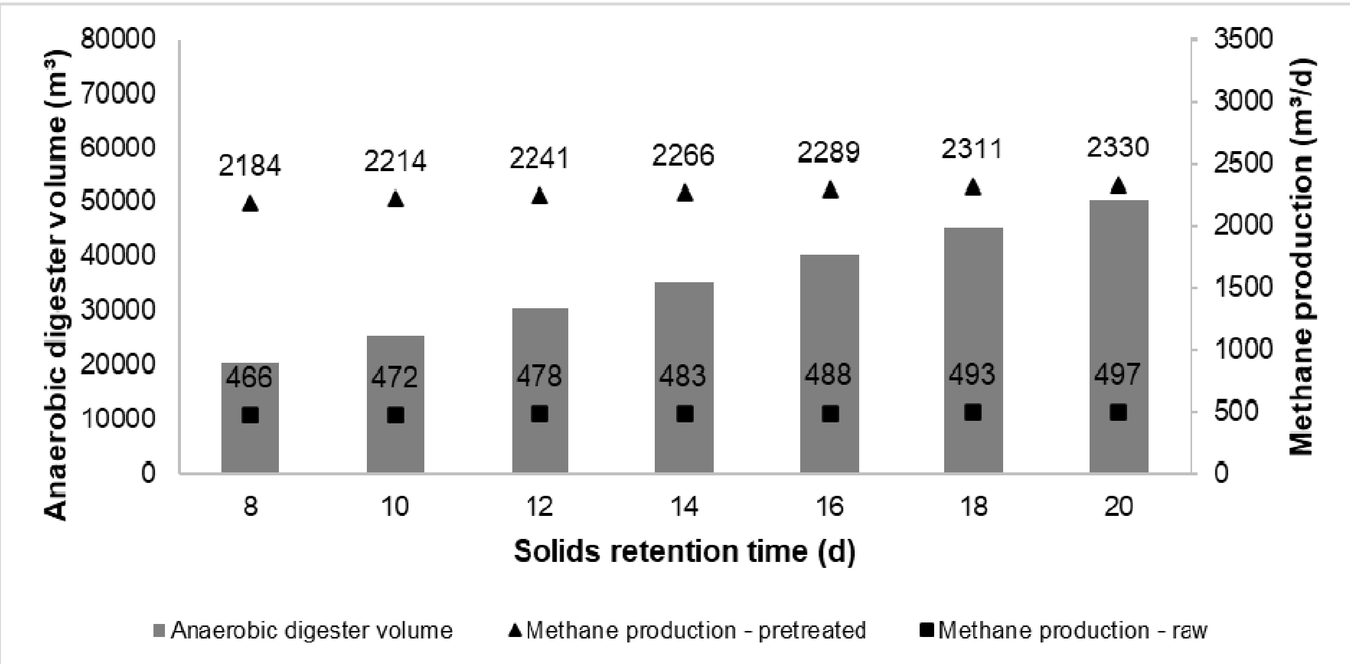

Fig. 2 Simulation of the anaerobic digestion process in a typical Brazilian bleached *Eucalyptus* kraft pulp mill, using raw and pretreated secondary sludge as substrate and considering 75% of the total exceeding sludge treated using anaerobic digestion.

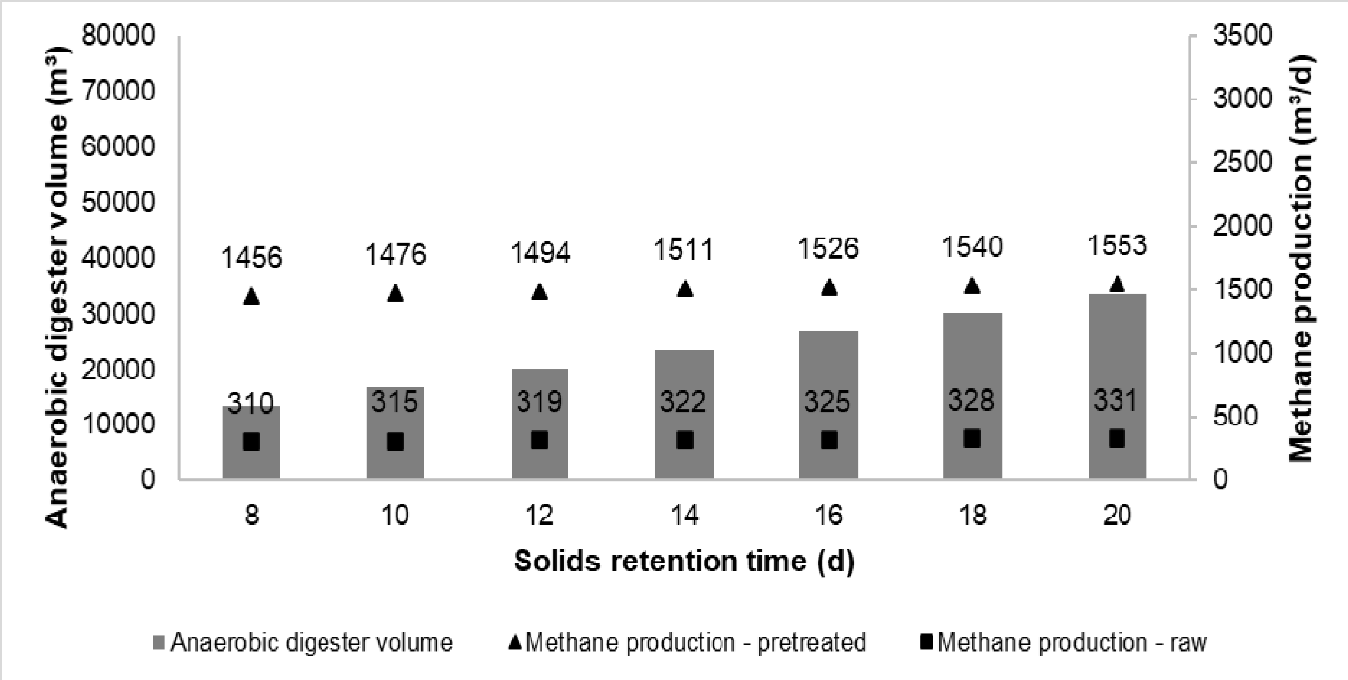

Fig. 3 Simulation of the anaerobic digestion process in a typical Brazilian bleached *Eucalyptus* kraft pulp mill, using raw and pretreated secondary sludge as substrate and considering 50% of the total exceeding sludge treated using anaerobic digestion.

The required anaerobic digester volume is greatly reduced when the sludge flow rate is diminished: to treat 75% of the sludge flow rate, a volume between 20160 and 50400 m³ is required; to treat 50% of the sludge flow, a volume between 13440 and 33600 m³ is needed.

The presence or absence of the pretreatment step was shown to be the most important factor for increasing the methane production and had a greater influence than the SRT. The best result for raw sludge was 662 m^3CH_4/d, when 100% of the total exceeding sludge was treated with an SRT of 20 d. Using pretreated sludge, this value was exceeded in all scenarios: 2912-3107 m^3CH_4/d (treating 100% of the sludge), 2184-2330 m^3CH_4/d (treating 75% of the sludge) and 1456-1553 m^3CH_4/d (treating 50% of the sludge). The results showed that pretreated sludge has a potential to produce 4.7 times more methane than raw sludge, when considering the same flow rate and SRT. This can be explained by the increase in the initial BOD as a result of the solubilization promoted by the pretreatment. Without pretreatment, not even a long SRT is sufficient to provide a significant increase in methane production.

Although the results only show a maximum potential for methane production and possibly overestimate the real methane yield, they provide an indication of the suitability of secondary sludge from P&P mills for anaerobic digestion and show that pretreatment was the major influence in the process.

The decision of whether or not to use a full-scale anaerobic digestion system has to consider the costs of implementation and maintenance, along with the benefits related to biogas production. In relation to a pretreatment plant coupled with the AD process, Li *et al*. (2019) presented a simple and useful tool for assessing process feasibility in terms of economic efficiency, using the cost of the input strategy and the price of the extra methane produced. According to their analysis, thermal pretreatment is one strategy classified as economically feasible.

Anaerobic digestion processes are highly applicable in Brazil, due to such favorable factors as operational simplicity and Brazilian climatic conditions, with high temperatures. In P&P mills, several opportunities can be considered. Biogas can be burned in a combined heat and power (CHP) plant to generate electricity and heat simultaneously. Considering the possible processes, a CHP system can produce heat for thermal pretreatment and anaerobic reactors, and also electrical power for the ETP. This can reduce the operating costs by providing power for pumps and aerators, making the effluent treatment plant a self-sufficient sector in terms of energy. The digested sludge has a potential for soil fertilization, due to its stabilized organic matter and high nutrient content, as described by Tambone *et al.* (2010). Another possibility is to use the available heat energy, commonly in the form of high-pressure steam generated in the recovery boiler, as the heat source for both the pretreatment and the anaerobic reactors, reducing the operating costs even more.

CONCLUSIONS

Different pretreatment techniques have been applied for the improvement of anaerobic digestion of pulp and paper sludge. Some of them, especially ultrasound and microwave, despite the increase in methane yield, are not currently favorable for full-scale implementation due the costs of construction, operation and maintenance, resulting in a negative energy balance. On the other hand, acid pretreatment was tested only once, and decreased the methane yield when compared with raw sludge.

Biological pretreatment, especially enzymatic options, showed difficulties for implementation, mainly because of the enzyme selection and the additional step of enzyme preparation. Because of this, the time required to perform the pretreatment is very high compared to the other processes, which can be a hindrance to full-scale implantation. Electrohydrolysis seems to be a good option for pretreatment, however more studies are necessary in order to verify the energy and economic issues.

The most promising pretreatments seems to be the thermal and thermal-alkaline processes. Both showed an increase in the methane production rate, generating more than 70% of the total methane in only 15-20 d. Also, a significant increase in the total amount of methane is achieved, with cases where more than 300% was produced when compared with raw sludge. Additionally, and considering sources of heat energy already existing inside the pulp mill itself, thermal pretreatment looks like the best option, considering the operating costs.

The case study allowed us to confirm the great influence of the pretreatment step on potential methane production. Using raw sludge, there is a maximum potential to produce 662 m^3CH_4/d, however pretreated sludge showed a potential between 1456-3107 m^3CH_4/d. The results provided an indication that P&P mill secondary sludge is suitable for anaerobic digestion, and that pretreatment was the major influence in the process, even more than some operating parameters like solids retention time.

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