**UNIVERSIDADE FEDERAL DE VIÇOSA**

**MARIELE FIOREZE**

# PRETREATMENT OF EUCALYPTUS KRAFT PULP MILL WASTE ACTIVATED SLUDGE TO ENHANCE ANAEROBIC DIGESTION

**VIÇOSA - MINAS GERAIS**
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Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Engenharia Civil, para obtenção do título de *Doctor Scientiae*.

Orientador: Claudio Mudadu Silva

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# RESUMO

FIOREZE, M., D.Sc., Universidade Federal de Viçosa, dezembro de 2021. **Pretreatment of eucalyptus kraft pulp mill waste activated sludge to enhance anaerobic digestion**. Orientador: Claudio Mudadu Silva.

O setor de produção de polpa celulósica e papel (P&P) é um dos maiores consumidores industriais de água e, em consequência, um dos maiores geradores de efluentes em todo o mundo. Nos processos de tratamento biológico aplicados aos efluentes, um grande volume de lodo biológico é gerado, o que resulta em altos custos de gerenciamento. Uma opção interessante para o gerenciamento do lodo é a digestão anaeróbia, capaz de reduzir o volume do lodo concomitantemente à geração de energia renovável que pode ser aproveitada nos processos industriais. No entanto, a digestão anaeróbia demanda melhorias tecnológicas e operacionais, principalmente devido ao elevado tempo de detenção hidráulica, da ordem de 30 a 40 dias, necessário para digerir o lodo de fábricas de P&P. A presente tese está dividida em 3 capítulos. O Capítulo 1 apresenta uma revisão da literatura sobre o potencial da digestão anaeróbia para o tratamento de lodos de fábricas de P&P, além da aplicação de métodos de pré-tratamento objetivando o aumento da produção de metano, a diminuição do tempo de detenção hidráulica e a diminuição do volume requerido aos digestores. É apresentado um estudo de caso, visando avaliar o potencial de integração das tecnologias de pré-tratamento e digestão anaeróbia de lodo biológico em uma típica fábrica de celulose kraft brasileira. A revisão da literatura resultou no encontro de 52 trabalhos publicados, sendo 16 artigos relacionados à digestão anaeróbia ou co-digestão de lodo de P&P sem pré-tratamento e 20 artigos relacionados à digestão anaeróbia de lodo de P&P após pré-tratamento. Foi verificada uma grande discrepância entre os resultados apresentados, o que dificultou nas avaliações e verificação dos reais impactos do pré-tratamento do lodo na viabilidade do sistema. Simulações foram realizadas usando dados atuais de uma fábrica de celulose kraft brasileira e demonstraram a grande influência do pré-tratamento na produção potencial de metano. O Capítulo 2 objetivou avaliar a aplicação de métodos de pré-tratamento térmicos, termo alcalinos e mecânicos, com o objetivo de promover a solubilização da matéria orgânica para potencializar a digestão anaeróbia. Os resultados demonstraram um ganho na solubilização, com um aumento superior a 1,2 vezes para DQO total, 7 vezes para DQO solúvel e 4 vezes para $DBO_5$. As condições de pré-tratamento termo alcalinas apresentaram os melhores resultados para todos os parâmetros avaliados, com a vantagem de requererem menores temperaturas e tempos de retenção quando comparado às condições térmicas. O Capítulo 3 teve como objetivo avaliar o potencial de produção de metano a partir do lodo biológico de uma fábrica de celulose kraft branqueada aplicando testes BMP (potencial bioquímico de metano). Após 30 dias, a produção acumulada de metano aumentou de 90 mL $CH_4$/gSV (lodo bruto) para 181-194 mL$CH_4$/gSV (pré-tratamento térmico) e 203-204 mL$CH_4$/gSV (pré-tratamento termo alcalino). A condição de pré-tratamento de 175 °C por 15 min em pH 11 foi suficiente para alcançar alta solubilização do lodo biológico e alta produção de metano. Os resultados demonstram que o pré-tratamento pode melhorar significativamente a digestão anaeróbia do lodo biológico da fábrica de celulose kraft, tornando a digestão anaeróbia uma opção atraente para o gerenciamento de lodo neste setor.

**Palavras-chave**: Digestão anaeróbia. Metano. Pré-tratamento. Papel e celulose. Lodo biológico.

# ABSTRACT

FIOREZE, M., D.Sc., Universidade Federal de Viçosa, December 2021. **Pretreatment of eucalyptus kraft pulp mill waste activated sludge to enhance anaerobic digestion**. Advisor: Claudio Mudadu Silva.

Pulp and paper (P&P) mills are currently one of the largest industrial water consumers and effluent generators worldwide. The biological effluent treatment processes currently in use generate a large volume of sludge (waste activated sludge – WAS), 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-day retention time required to digest pulp mill sludge in conventional anaerobic bioreactors. The thesis was structured in 3 chapters written as scientific papers. Chapter 1 presented a literature review about 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 presented results made it difficult to assess the suitability of anaerobic digestion and the actual impacts of the sludge pretreatment on the viability of the system. 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. Chapter 2 aimed the application of thermal, thermal-alkaline and mechanical pretreatment methods in order to promote the solubilization of organic matter to enhance the anaerobic digestion. Chemical analyses showed an improvement in organic matter solubilization, with an increase greater than 1.2-fold for total COD, 7-fold for soluble COD and 4-fold for $BOD_5$. In general, thermal-alkaline pretreatment showed the best results for all the evaluated parameters, with the advantage of requiring lower temperature and retention time when compared to thermal conditions. Chapter 3 aimed to evaluate the potential of methane production from the WAS of a bleached kraft pulp mill applying biochemical methane potential (BMP). After 30 days of testing, cumulative methane production increased from 90 mL

$CH_4$/gVS (raw sludge) to 181-194 mL $CH_4$/gVS with thermally pretreated samples, and up to 203-204 mL $CH^4$/gVS with samples which were pretreated using the thermo-alkaline technique. The pretreatment conditions of 175 °C for 15 min at pH 11 were sufficient to achieve both a high solubilization of WAS and a high methane production. The results showed that pretreatment could significantly enhance the anaerobic digestion of kraft pulp mill WAS, making this an attractive new option for sludge management in this sector.

**Keywords**: Anaerobic digestion. Methane yield. Pretreatment. Pulp and paper mill. Secondary sludge.

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## LISTA DE ABREVIATURAS E SIGLAS

| | | | |
|---|---|---|---|
| BMP | | Potencial bioquímico de metano | *Biochemical methane potential* |
| BMPth | | Potencial teórico bioquímico de metano | *Theoretical biochemical methane potential* |
| $CH_4$ | | Gás metano | *Methane* |
| CHP | | Sistema combinado de calor e eletricidade | *Combined heat and power plant* |
| CSTR | | Reator tipo tanque agitado | *Continuously Stirred Tank Reactor* |
| DA | AD | Digestão anaeróbia | *Anaerobic digestion* |
| $DBO_5$ | $BOD_5$ | Demanda bioquímica de oxigênio | *Biochemical oxygen demand* |
| DBOu | BODu | Demanda bioquímica de oxigênio última | *Ultimate biochemical oxygen demand* |
| DQOt | tCOD | Demanda química de oxigênio total | *Total chemical oxygen demand* |
| DQOs | sCOD | Demanda química de oxigênio total | *Soluble chemical oxygen demand* |
| ETE | ETP | Estação de tratamento de efluentes | *Effluent treatment plant* |
| LP | PS | Lodo primário | *Primary sludge* |
| LS | SS | Lodo secundário | *Secondary sludge* |
| $N\text{-}NH_3$ | $NH_3\text{-}N$ | Nitrogênio amoniacal | *Ammonia-nitrogen* |
| NTK | TKN | Nitrogênio total kjeldahl | *Total kjeldahl nitrogen* |
| P | | Fósforo | *Phosphorus* |
| P&P | | Polpa celulósica e papel | *Pulp and paper* |
| ST | TS | Sólidos totais | *Total solids* |
| SV | VS | Sólidos voláteis | *Volatile solids* |
| TDH | HRT | Tempo de detenção hidráulico | *Hydraulic retention time* |
| TSA | ADt | Tonelada de polpa seca ao ar | *Air-dried ton of pulp* |
| | WAS | | *Waste activated sludge* |

**SUMÁRIO**

# INTRODUÇÃO GERAL

O Brasil é um dos destaques mundiais no ramo de produção de polpa celulósica e papel (P&P). Com uma produção anual de cerca de 21 milhões de toneladas de polpa e 10 milhões de toneladas de papel (Ibá, 2018), se caracteriza como um dos principais países do ramo. Essa atividade possui estreita vinculação com o meio ambiente, sobretudo devido aos elevados índices relacionados ao consumo de água, geração de efluentes líquidos e resíduos sólidos e emissões atmosféricas.

Um dos reflexos do elevado volume de efluentes é a geração de lodos como resultado dos processos de tratamento. Tradicionalmente, estes são desaguados e, majoritariamente, dispostos em aterros ou, em alguns casos, incinerados ou compostados (Kamali *et al.*, 2016). Apesar de serem ambientalmente aceitas, essas alternativas representam elevados custos, além de coibirem o potencial dos lodos para a geração de biogás. O desenvolvimento e aprimoramento de modelos mais sustentáveis para o gerenciamento de tais resíduos, que sejam eficientes para o tratamento ao mesmo tempo em que resultem em menores gastos ou mesmo em algum tipo de benefício para a indústria, se torna imprescindível.

Há um crescente interesse no estudo da digestão anaeróbia. Porém, pesquisas indicam a necessidade de altos tempos de detenção hidráulica (TDH) para uma geração satisfatória de biogás, requerendo, portanto, reatores com elevados volumes, o que torna o processo economicamente pouco atraente (Meyer & Edwards, 2014; Kamali *et al.*, 2016). A digestão anaeróbia precedida por algum método de pré-tratamento que contribua para a solubilização prévia da matéria orgânica tem sido proposta. Diversos trabalhos apresentam resultados promissores ao estudarem métodos de pré-tratamento químicos, físicos e/ou biológicos, com ganhos relacionados ao aumento da produção final de metano e aceleração do processo, ou seja, lodos pré-tratados não só produzem mais metano como o fazem mais rapidamente (Meyer & Edwards, 2014; Kamali *et al.*, 2016). Potencialmente, o biogás gerado pode ser utilizado para a geração de calor e/ou energia e sustento de outras operações dentro da própria unidade fabril.

Uma fábrica típica de polpa celulósica *kraft* gera parte, quando não, toda a energia necessária para o sustento das atividades fabris, por meio da queima de subprodutos da madeira na caldeira de biomassa e do licor preto concentrado na caldeira de recuperação química. Em muitos casos, as fábricas geram um excedente de energia que acaba sendo vendido, representando uma significativa fonte de lucros. A produção de energia a partir da digestão anaeróbia de lodos é uma opção, sobretudo para suprimento da demanda energética da estação de tratamento de efluentes (ETE), conforme experiências em estações de tratamento de efluentes municipais (Gomes *et al*., 2017). Além disso, a melhoria na gestão de resíduos e o aumento da oferta de energia sustentável visando diminuir a dependência dos combustíveis fósseis em território nacional são objetivos previstos na Lei Federal n. 13.576/2017 – *RenovaBio* (Brasil, 2017).

O presente estudo visou compreender os efeitos de diferentes métodos de pré-tratamento na solubilização de lodos biológicos de fábrica de polpa celulósica *kraft* branqueada e na posterior geração de metano em ensaios laboratoriais que simulam a digestão anaeróbia.

No Capítulo 1 é apresentada uma revisão da literatura, tratando dos aspectos de geração e características de lodos em fábricas de polpa celulósica e papel, potencial para digestão anaeróbia e métodos de pré-tratamento já estudados. São apresentados e comparados trabalhos publicados ao redor do mundo, os quais aplicam ou não alguma técnica para solubilização prévia do lodo anteriormente à digestão anaeróbia. Por fim, são apresentadas simulações com dados de uma indústria brasileira de polpa celulósica *kraft* branqueada, comparando os efeitos da presença/ausência de pré-tratamento no volume requerido ao digestor anaeróbio e na produção de metano.

No Capítulo 2 são apresentados e discutidos os ensaios de pré-tratamento realizados para a solubilização de lodos biológicos, com foco na solubilização da matéria orgânica e incremento do potencial teórico de geração de metano. Foram testados os pré-tratamentos térmico, térmico-alcalino e mecânico, em 16 diferentes condições operacionais, com vista a determinar as melhores condições para os posteriores ensaios laboratoriais de produção de metano (BMP). Os testes foram realizados junto ao Laboratório de Celulose e Papel (LCP) da Universidade Federal de Viçosa (UFV).

No Capítulo 3 são abordados os aspectos metodológicos, resultados e discussões acerca dos ensaios laboratoriais para mensuração do potencial bioquímico de metano (BMP), utilizando as amostras pré-tratadas que apresentaram os melhores resultados de solubilização e de lodo não pré-tratado (bruto) para fins de comparação dos resultados. Os ensaios BMP foram realizados junto ao Laboratório de Química Tecnológica e Ambiental (LQTA) da Universidade Federal de Ouro Preto (UFV).

## HIPÓTESES DA PESQUISA

A presente pesquisa foi conduzida sob as seguintes hipóteses:

i. os métodos de pré-tratamento *térmico*, *térmico-alcalino* e *mecânico*, aplicados a lodos biológicos oriundos do tratamento de efluentes de fábrica de polpa celulósica *kraft* branqueada, promovem a solubilização do lodo, com incremento do teor de matéria orgânica solúvel passível de contribuir com a geração de metano;

ii. lodos previamente solubilizados pela ação do pré-tratamento produzem significativamente mais metano quando comparados a lodos não pré-tratados (lodo bruto), considerando testes conduzidos em batelada, em escala de bancada;

iii. a digestão anaeróbia do lodo biológico pode ser economicamente viável quando aplicados os devidos métodos de pré-tratamento e em condições operacionais adequadas, sendo uma opção a ser considerada pela indústria para o gerenciamento de tais resíduos.

# OBJETIVOS

## Objetivo geral

O presente trabalho visou testar a aplicação de diferentes métodos de pré-tratamento e sob diferentes condições operacionais no intuito de potencializar a digestão anaeróbia de lodos originados no tratamento biológico de efluentes da indústria de fabricação de polpa celulósica *kraft* branqueada.

## Objetivos específicos

i. estudar e comparar os avanços até então apresentados pela literatura científica publicada, em relação à: lodo utilizado (primário, secundário ou misto), métodos de pré-tratamento com maior potencial para incremento da produção de metano e aspectos econômicos e energéticos;

ii. verificar os impactos dos métodos de pré-tratamento *térmico*, *térmico-alcalino* e *mecânico*, em distintas condições operacionais, na solubilização do lodo biológico;

iii. mensurar a produção de metano de lodos pré-tratados e compará-la com aquela alcançada por lodo não pré-tratado (produção final acumulada e produção parcial);

iv. gerar recomendações para a indústria a fim de auxiliar no avanço da tecnologia para implantação em escala real.

# CHAPTER 1

## 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

# 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

**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 53 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.

# 1 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 employed pulping process, the raw material and the applied effluent treatment technique. 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.

## 2 MATERIAL AND METHODS

### 2.1 Literature search and analysis

The review method was carried out based on the eight-step proposal of Okoli & Schabram (2010). To determine the purpose of the review, 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 discussed.

## 2.2 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 an 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 obtain the 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% (Metcalf & Eddy, 2013).

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 surplus activated 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-year 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).

## 3. RESULTS AND DISCUSSION

### 3.1 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.

### 3.2 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).

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

| **Methane yield ($mLCH_4/gVS$)** | | | | | **Reference** |
|---|---|---|---|---|---|
| **Primary sludge** | **Secondary sludge** | **Mixed sludge** | **Co-digestion** | **Lake sedimented fiber** | |
| - | - | 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 & Rintala, 2012 |
| - | - | - | 0.25[(2)] | - | Parameswaran & Rittmann, 2012 |
| - | 53 | - | 80 | - | Hagelqvist, 2013a |
| - | - | - | 432 | - | Lin *et al.*, 2013 |
| - | - | - | 183 | - | Huilinir *et al.*, 2014 |
| - | - | 230 | - | - | Ekstrand *et al.*, 2016 |
| - | - | - | 50 | - | Hagelqvista & 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)] $L\ CH_4/L_{reactor}.d$

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 effluents from a sulfite pulp mill from the 1910s to the 1980s, and has been estimated to contain about 1.5 million $m^3$ 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.

### 3.3 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.

**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 | | | | | | Reference |
|---|---|---|---|---|---|---|
| **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 |

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).

Thermal hydrolysis also resulted in an important improvement in the rate of methane production. Wood *et al.* (2009) generated approximately 220 mL$CH_4$/gCOD after 15 d, 250 mL$CH_4$/gCOD after 20 d and 300 mL$CH_4$/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 mL$CH_4$/gCOD after 15 d, 125 mL$CH_4$/gCOD after 20 d and 200 mL$CH_4$/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 for COD solubilization and methane production. According to the authors (Bayr *et al.*, 2013), this could be due to ammonia inhibition as $HNO_3$ acid was used for acid pretreatment, resulting on the inhibition of hydrolysis as demonstrated by the long lag phase (25 d) and the low methane production rates.

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® is a technology that combines chemical and mechanical disintegration for the 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.

### 3.4 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 (see the Appendix A, Table S1). The scenarios evaluated included: 50% (1680 m³/d), 75% (2520 m³/d) and 100% (3360 m³/d) of the total surplus activated 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%, $BOD_5$ 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 | 7549±173 mg/L | 10,823±552 mg/L |
| sCOD | 1112±22 mg/L | 10,729±492 mg/L |
| $BOD_5$ | 570±34 mg/L | 2765±36 mg/L |
| BODu | 856±97 mg/L | 4015±235 mg/L |

Figures 1, 2 and 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 surplus activated sludge was treated using anaerobic digestion, the necessary digester volume increased 2.5 times, from 26,880 m³ (SRT of 8 d) to 67,200 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.

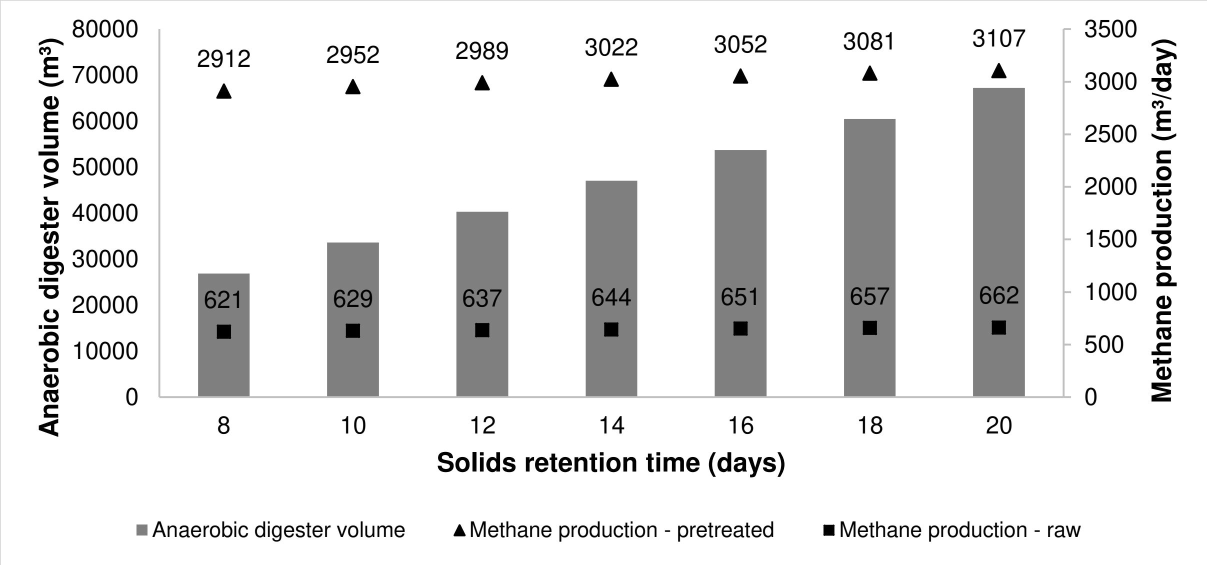


**Figure 1**. Simulation of the anaerobic digestion process in a typical Brazilian bleached eucalyptus kraft pulp mill, using raw and pretreated secondary sludge as substrate and considering 100% of the surplus activated sludge treated with anaerobic digestion

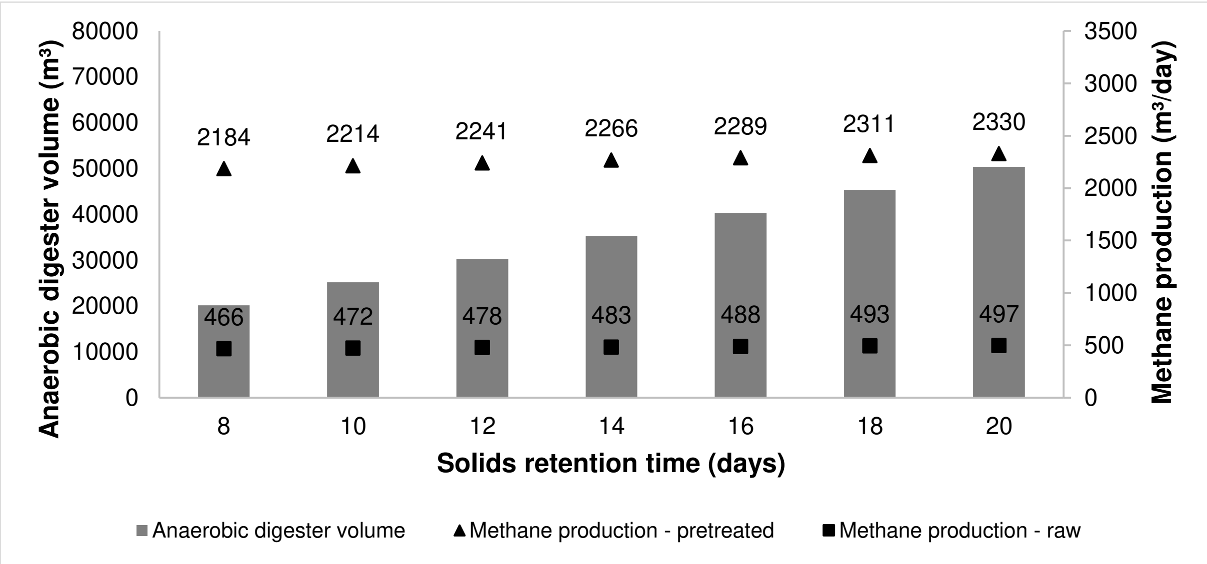


**Figure 2**. Simulation of the anaerobic digestion process in a typical Brazilian bleached eucalyptus kraft pulp mill, using raw and pretreated secondary sludge as substrate and considering 75% of the surplus activated sludge treated using anaerobic digestion

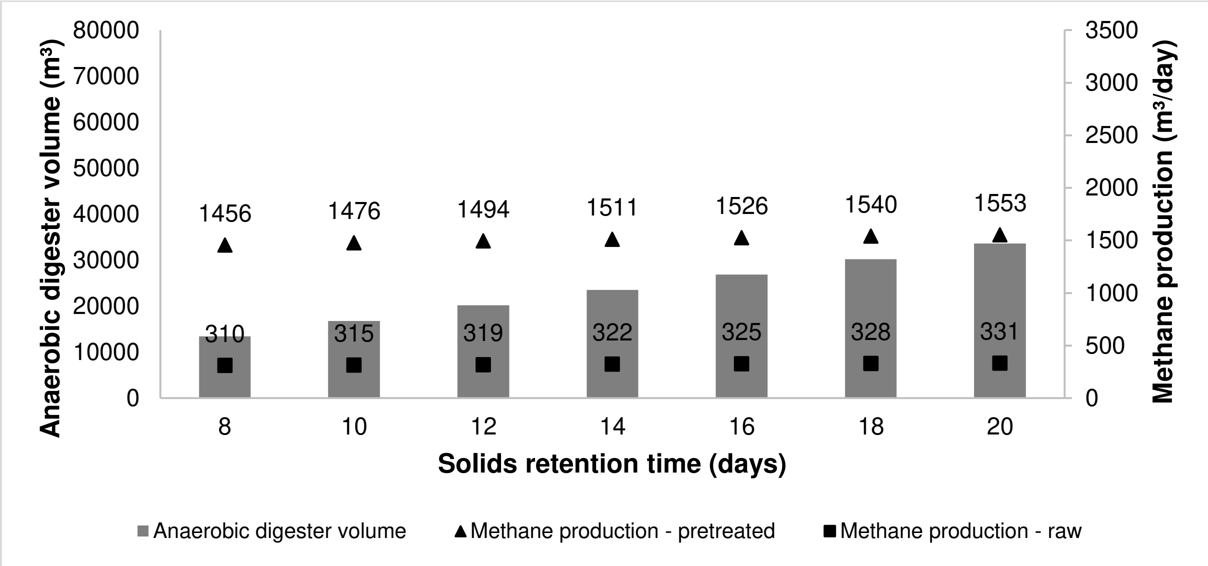


**Figure 3**. Simulation of the anaerobic digestion process in a typical Brazilian bleached eucalyptus kraft pulp mill, using raw and pretreated secondary sludge as substrate and considering 50% of the surplus activated sludge treated using anaerobic digestion

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 m³$CH_4$/d, when 100% of the surplus activated sludge was treated with an SRT of 20 d. Using pretreated sludge, this value was exceeded in all scenarios: 2912-3107 m³$CH_4$/d (treating 100% of the sludge), 2184-2330 m³CH4/d (treating 75% of the sludge) and 1456-1553 m³$CH_4$/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.

## 4 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.

**REFERENCES**

APHA, AWWA, WPC. (2012) *Standard methods for the examination of water and wastewater*. 22. ed. Washington: American Public Health Association, American Water Works Association, Water Environment Federation.

Bayr, S. & Rintala, J. (2012) Thermophilic anaerobic digestion of pulp and paper mill primary sludge and co-digestion of primary and secondary sludge. *Water Research* **46**(15), 4713–4720.

Bayr, S. (2014) Biogas Production from Meat and Pulp and Paper Industry By-Products. Master Thesis, University of Jyväskylä, Finland.

Bayr, S., Kaparaju, P. & Rintala, J. (2013) Screening pretreatment methods to enhance thermophilic anaerobic digestion of pulp and paper mill wastewater treatment secondary sludge. *Chemical Engineering Journal* **223**, 479–486.

Bolzonella, D., Pavan, P., Battistoni, P. & Cecchi, F. (2005) Mesophilic anaerobic digestion of waste activated sludge: influence of the solid retention time in the wastewater treatment process. *Process Biochemistry* **40**, 1453–1460.

Boman, B. & Bergström, R. (1985) Anaerobic treatment of fibre sediment and forest industry waste sludge. *Institutet foer Vatten- och Luftvaardsforskning*, 792.

Bonilla, S., Choolaei, Z., Meyer, T., Edwards, E.A., Yakunin, A.F. & Allen, D.G. (2018) Evaluating the effect of enzymatic pretreatment on the anaerobic digestibility of pulp and paper biosludge. *Biotechnology Reports* **17**, 77-85.

Chakraborty, D., Shelvapulle, S., Reddy, K.R., Kulkarni, R.V., Puttaiahgowda, Y.M., Naveen, S. & Raghu, A.V. (2019) Integration of biological pre-treatment methods for increased resource replace resource with energy recovery from paper and pulp biosludge. *Journal of Microbiological Methods* **160**, 93-100.

Chatterjee, P., Lahtinen, L., Kokko, M. & Rintala, J. (2018) Remediation of sedimented fiber originating from pulp and paper industry: Laboratory scale anaerobic reactor studies and ideas of scaling up. *Water Research* **143**(15), 209-217.

Coimbra, R.N., Paniagua, S., Escapa, C., Calvo, L.F. & Otero, M. (2015) Combustion of primary and secondary pulp mill sludge and their respective blends with coal: A thermogravimetric assessment. *Renewable Energy* **83**, 1050-1058.

Ekstrand, M.-E., Karlsson, M., Truong, X.-B., Björn, A., Karlsson, A., Svensson, B.H. & Ejlertsson, J. (2016) High-rate anaerobic co-digestion of kraft mill fibre sludge and activated sludge by CSTRs with sludge recirculation. *Waste Management* **56**, 166-172.

Elliott, A. & Mahmood, T. (2007) Pretreatment technologies for advancing anaerobic digestion of pulp and paper biotreatment residues. *Water Research* **41**(19), 4273–4286.

Elliott, A. & Mahmood, T. (2012) Comparison of Mechanical Pretreatment Methods for the Enhancement of Anaerobic Digestion of Pulp and Paper Waste Activated Sludge. *Water Environment Research* **84**(6), 497–505.

Gomez, X., Cuetos, M.J., Garcıa, A.I. & Moran, A. (2005) Evaluation of digestate stability from anaerobic process by thermogravimetric analysis. *Thermochim. Acta* **426**, 179-184.

Gottumukkala, L.D., Haigh, K., Collard, F.X., Rensburg, E.R. & Görgens, J. (2016) Opportunities and prospects of biorefinery-based valorisation of pulp and paper sludge. *Bioresource Technology* **215**, 37-49.

Grosser, A. & Celary, P. (2019) Biogas (methane production) and energy recovery from different sludges. *Emerging Concerns and Scope for Resource Recovery*, 705-740.

Hagelqvist, A. & Granström, K. (2016) Co-digestion of manure with grass silage and pulp and paper mill sludge using nutrient additions. *Environmental Technology* **37**, 2113-2123.

Hagelqvist, A. (2013a) Batchwise mesophilic anaerobic co-digestion of secondary sludge from pulp and paper industry and municipal sewage sludge. *Waste Management* **33**(4), 820–824.

Hagelqvist, A. (2013b) Sludge from pulp and paper mills for biogas production treatment and sludge management Sludge from pulp and paper mills for biogas production Strategies to improve energy performance in wastewater. PhD Thesis, Karlstad University, Sweden.

Hanum, F., Yuan, L.C., Kamahara, H., Aziz, H.A., Atsuta, Y., Yamada, T. & Daimon, H. (2019) Treatment of Sewage Sludge Using Anaerobic Digestion in Malaysia: Current State and Challenges. *Frontiers in Energy Research*.

Huang, X. M. (2015) Enhancing Anaerobic Digestion of Pulp and Paper Mill Biosludge using Thermal Treatment in a Bench-scale System.  MSSASc Thesis, Uiversity of Toronto, Canada.

Huiliñir, C., Quintriqueo, A., Antileo, C. & Montalvo, S. (2014) Methane production from secondary paper and pulp sludge: Effect of natural zeolite and modeling. *Chemical Engineering Journal* v. **257**, 131-137.

Hynninen, P. (2008) Effluent treatment. In: Dahl O, editor. *Environmental management and control*. 1st Ed. Paperi ja Puu Oy; Helsinki; pp. 86-116.

Jokela, J., Rintala, J., Oikari, A., Reinikainen, O., Mutka, K. & Nyronen, T. (1997) Aerobic composting and anaerobic digestion of pulp and paper mill sludges. *Water Science & Technology*, v. **36**(11), 181-188.

Kamali, M, Gameiro, T., Costa, M.E.V. & Capela, I. (2016) Anaerobic digestion of pulp and paper mill wastes – An overview of the developments and improvement opportunities. *Chemical Engineering Journal*, **298**(15), 162-182.

Karlsson, A., Truong, X.B., Gustavsson, J., Svensson, B.H., Nilsson, F. & Ejlertsson, J. (2011) Anaerobic treatment of activated sludge from Swedish pulp and paper mills – biogas production potential and limitations. *Environmental Technology* **32**(14), 1559–1571.

Karlsson, R. (2010) Anaerobic digestion of biological sludge from the pulp and paper industry. MSc Thesis, Linköping University, Linköping, Sweden.

Kinnunen, V., Yla-Outinen, A. & Rintala, J. (2015) Mesophilic anaerobic digestion of pulp and paper industry biosludgeelong-term reactor performance and effects of thermal pretreatment. *Water Research* **87**, 105-111.

Kokko, M., Koskue, V. & Rintala, J. (2018) Anaerobic digestion of 30-100-year-old boreal lake sedimented fiber from the pulp industry: Extrapolating methane production potential to a practical scale. *Water Research* **133**, 218-226.

Kolbl, S., Forte-Tavcer, P. & Stres, B. (2017) Potential for valorization of dehydrated paper pulp sludge for biogas production: Addition of selected hydrolytic enzymes in semicontinuous anaerobic digestion assays. *Energy* **126,** 326-334.

Lackey, J.C., Peppley, B., Champagne, P. & Maier, A. (2015) Composition and uses of anaerobic digestion derived biogas from wastewater treatment facilities in North America. *Waste Management & Research* **33**(8), 767–771.

Li, Y., Chen, Y. & Wu, J. (2019) Enhancement of methane production in anaerobic digestion process: A review. *Applied Energy* **240**, 120–137.

Lin, Y., Liang, J., Zeng, C., Wang, D. & Lin, H. (2017) Anaerobic digestion of pulp and paper mill sludge pretreated by microbial consortium OEM1 with simultaneous degradation of lignocellulose and chlorophenols. *Renewable Energy* **108**, 108–115.

Lin, Y., Wang, D. & Wang, L. (2010) Biological pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge. *Waste Management & Research* **28**(9), 800–810.

Lin, Y., Wang, D., Li, Q. & Xiao, M. (2011) Mesophilic batch anaerobic co-digestion of pulp and paper sludge and monosodium glutamate waste liquor for methane production in a bench-scale digester. *Bioresource Technology* **102**(4), 3673–3678.

Lin, Y., Wang, D., Wu, S. & Wang, C. (2009) Alkali pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge. *Journal of Hazardous Materials* **170**(1), 366–373.

Lin, Y., Wu, S. & Wang, D. (2013) Hydrogen-methane production from pulp & paper sludge and food waste by mesophilic-thermophilic anaerobic co-digestion. *International Journal of Hydrogen Energy* **38**(35), 15055–15062.

Lopes, A.C.P. (2017) Biogas production potential from kraft pulp mill sludge. Master Thesis, Universidade Federal de Viçosa, Viçosa, Brazil.

Lopes, A.C.P., Silva, C.M., Rose, A.P. & Rodrigues, F.A. (2018) Biogas production from thermophilic anaerobic digestion of kraft pulp mill sludge. *Renewable Energy* **124**, 40-49.

Mahmood, T. & Elliot, A. (2016) A review of secondary sludge reduction technologies for the pulp and paper industry. *Water Research* **40**, 2093–2112.

Mäkelä, M., Benavente, V. & Fullana, A. (2016) Hydrothermal carbonization of industrial mixed sludge from a pulp and paper mill. *Bioresource Technology* **200**, 444–450.

Manesh, M. E. (2012) Utilization of Pulp and Paper Mill Sludge as Filler in Nylon Biocomposite Production. PhD Thesis, University of Toronto, Canada.

Mehdizadeh, S.N., Eskicioglu, C., Milani, A.S. & Saha, M. (2012) Empirical modeling of the effects of emerging pretreatment methods on anaerobic digestion of pulp mill biosolids. *Biochemical Engineering Journal* **68**, 167-177.

Metcalf & Eddy, Inc. *Wastewater Engineering Treatment and Reuse* (Fourth Edition) George Tchobanoglous Franklin L. Burton H. David Stensel. McGraw Hill, 2013.

Meyer, T. & Edwards, E.A. (2014) Anaerobic digestion of pulp and paper mill wastewater and sludge. *Water Research* **65**, 321–349.

Nosek, R., Holubcik, M., Jandacka, J. & Radacovska, L. (2017) Analysis of Paper Sludge Pellets for Energy Utilization. *Bioresources* **12**(4), 7032-7040.

O'Brien, T., Herbert, S. & Barker, A. (2002) Growth of corn in varying mixtures of paper mill sludge and soil. *Commun Soil Sci Plan* **33**(3-4), 635-46.

Okoli, C. & Schabram, K. (2010) A Guide to Conducting a Systematic Literature Review of Information Systems Research. *Sprouts: Working Papers on Information Systems* **10**(26).

Parameswaran, P. & Rittmann, B.E. (2012) Feasibility of anaerobic co-digestion of pig waste and paper sludge. *Bioresource Technology* **124**, 163-168.

Park, N.D., Helle, S.S. & Thring, R.W. (2012) Combined alkaline and ultrasound pre-treatment of thickened pulp mill waste activated sludge for improved anaerobic digestion. *Biomass and Bioenergy* **46**, 750–756.

Pontual, L., Mainier, P.B. &Lima, G.B. (2015) The Biogas Potential of Pulp and Paper Mill Wastewater: An Essay. *American Journal of Environmental Engineering* **5**(3), 53-57.

Priadi, C., Wulandari, D., Rahmatika, I. & Moersidik, S. (2013) Biogas production in the anaerobic digestion of paper sludge. In *5th International Conference on Chemical*, Biological and Environmental Engineering – ICBEE.

Puhakka, J.A., Alavakeri, M. & Shieh, W.K. (1992) Anaerobic treatment of kraft pulp-mill waste activated-sludge: Gas production and solids reduction. *Bioresource Technology* **39**(1), 61–68.

Puhakka, J.A., Viitasaari, M.A., Latola, P.K. & Määttä, R.K. (1988) Effect of Temperature on Anaerobic Digestion of Pulp and Paper Industry Wastewater Sludges. *Water Science & Technology* **20**(1), 193–201.

Reckamp, J.M., Garrido, R.A. & Satrio, J.A. (2014) Selective pyrolysis of paper mill sludge by using pretreatment processes to enhance the quality of bio-oil and biochar products. *Biomass and Bioenergy* **71**, 235-244.

Reeve, D.W. & Silva, C.M. (2000) *Chemical Pulping*, 1 ed., vol. B; Gullichsen, J.; Fogelholm, C. J., eds.; Fapet Oy: Helsinki, chapter 22, p. 441.

Rintala, J.A. & Puhakka, J.A. (1994) Anaerobic treatment in pulp- and paper-mill waste management: A review. *Bioresource Technology* **47**(1), 1-18.

Saha, M., Eskicioglu, C. & Marin, J. (2011) Microwave, ultrasonic and chemo-mechanical pretreatments for enhancing methane potential of pulp mill wastewater treatment sludge. *Bioresource Technology* **102**(17), 7815–7826.

Sethupathy, A. & Sivashanmugam, P. (2018) Enhancing biomethane potential of pulp and paper sludge through disperser mediated polyhydroxyalkanoates. *Energy Conversion and Management* **173**, 179-186.

Sethupathy, A., Arun, C., Sivashanmugam, P. & Kumar, R.R. (2020) Enrichment of biomethane production from paper industry biosolid using ozonation combined with hydrolytic enzymes. *Fuel* **279**, 118522.

Simão, L., Hotza, D., Raupp-Pereira, F., Labrincha, J.A. & Montedo, O.R.K. (2018) Wastes from pulp and paper mills - a review of generation and recycling alternatives. *Cerâmica* **64**(371).

Stoica, A., Sandberg, M. & Holby, O. (2009) Energy use and recovery strategies within wastewater treatment and sludge handling at pulp and paper mills. *Bioresource Technology* **100**(14), 3497–3505.

Tambone, F., Scaglia, B., D'Imporzano, G., Schievano, A., Orzi, V., Salati, S. & Adani, F. (2010) Assessing amendment and fertilizing properties of digestates from anaerobic digestion through a comparative study with digested sludge and compost. *Chemosphere* **81**, 577–583.

Tiseo. I. (2021) Global market value of paper and pulp 2019 & 2024. Jan 27, 2021. https://www.statista.com/statistics/1073451/global-market-value-pulp-and-paper/

Tyagi, V.K., Lo, S.L. & Rajpal, A. (2014) Chemically coupled microwave and ultrasonic pre-hydrolysis of pulp and paper mill waste-activated sludge: Effect on sludge solubilisation and anaerobic digestion. *Environmental Science and Pollution Research* **21**(9), 6205–6217.

USEPA (2013). *Handbook for Sampling and Sample Preservation of Water and Wastewater*, U.S. Environmental Protection Agency, Cincinnati, OH, USA

Veluchamy, C. & Kalamdhad, A.S. (2017a) Influence of pretreatment techniques on anaerobic digestion of pulp and paper mill sludge: A review. *Bioresource Technology* **245**(A), 1206-1219.

Veluchamy, C. & Kalamdhad, A.S. (2017b) Biochemical methane potential test for pulp and paper mill sludge with different food/microorganisms ratios and its kinetics. *International Biodeterioration & Biodegradation* **117**, 197-204.

Veluchamy, C., Raju, V.W. & Kalamdhad, A.S. (2017) Prerequisite – an electrohydrolysis pretreatment for anaerobic digestion of lignocellulose waste material. *Bioresource Technology* **235**, 274–280.

Veluchamy, C., Raju, V.W. & Kalamdhad, A.S. (2018) Electrohydrolysis pretreatment for enhanced methane production from lignocellulose waste pulp and paper mill sludge and its kinetics. *Bioresource Technology* **252**, 52-58.

Wood, N., Tran, H. & Master, E. (2009) Pretreatment of pulp mill secondary sludge for high-rate anaerobic conversion to biogas. *Bioresource Technology* **100**(23), 5729–5735.

Wood, N., Tran, H. & Master, E. (2010) Improving anaerobic conversion of pulp mill secondary sludge to biogas by pretreatment. *Tappi Journal*, June, 16–21.

Zhang, J., Wang, S., Lang, S., Xian, P. & Xie, T. (2016) Kinetics of combined thermal pretreatment and anaerobic digestion of waste activated sludge from sugar and pulp industry. *Chemical Engineering Journal* **295**, 131-138.

Zhang, L., Champagne, P. & Xu, C.C. (2011) Bio-crude production from secondary pulp/paper-mill sludge and waste newspaper via co-liquefaction in hot-compressed water. *Energy* **36**(4), 2142-2150.

# CHAPTER 2

## EFFECTS OF PRETREATMENTS ON THE SOLUBILIZATION AND THEORETICAL METHANE PRODUCTION OF WASTE ACTIVATED SLUDGE FROM A BRAZILIAN EUCALYPTUS KRAFT PULP MILL

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**Abstract**

Waste activated sludge (WAS) originating from kraft pulp mill effluent treatment plants represents an important environmental challenge for this industry. Anaerobic digestion is a promising option for WAS treatment, with the added benefit of biogas production. This paper presents the application of thermal, thermal-alkaline, and mechanical pretreatment methods in order to promote the solubilization of organic matter to enhance the anaerobic digestion of the WAS from a Brazilian eucalyptus bleached kraft pulp mill. A total of 16 pretreatment operating conditions were compared. Chemical analyses showed an improvement in organic matter solubilization, with an increase greater than 7-fold for soluble chemical oxygen demand and 4-fold for biochemical oxygen demand. Nutrient solubilization showed an increase greater than 10-fold for total *Kjeldahl* nitrogen and 3-fold for total phosphorus. Theoretical biochemical methane potential was improved from 211 $mLCH_4/gVS$ for raw sludge to 333-343 $mLCH_4/gVS$ after mechanical pretreatment, 314-360 $mLCH_4/gVS$ after thermal pretreatment, and 373-378 $mLCH_4/gVS$ after thermal-alkaline pretreatment. In general, thermal-alkaline pretreatment showed the best results for all the evaluated parameters, with the advantage of requiring lower temperature and retention time when compared to thermal conditions.

**Keywords**: Anaerobic digestion; Biogas; Pretreatment; Pulp and paper mill; Sludge digestion.

# 1 INTRODUCTION

In addition to consuming significant quantities of fresh water, the pulp and paper (P&P) industry is one of the world´s largest generators of effluents. Despite the continuous reduction of water use, from about 200 $m^3$/ADT in the 1960's to the current 25 $m^3$/ADT in modern kraft pulp mills, an average of approximately 60 $m^3$/ADT of effluent is generated (Reeve *et al.* 2000; Karlsson 2010).

Effluent treatment plants (ETP) generate considerable amounts of waste activated sludge (WAS), which is usually incinerated or disposed of in landfills. Sludge generation in Canadian mills was estimated at 50 kg/ADT, and WAS corresponds to approximately 30% of this total (Elliot and Mahmood 2005). Sludge management represents a large financial burden on P&P mills. Approximately 60% of the total effluent treatment costs are spent on sludge management and disposal (Kamali *et al.* 2016). Therefore, there is a growing demand for methods that minimize the costs by reducing the volume of WAS or reducing the cost of the treatment and final disposal.

Anaerobic digestion is a promising treatment for WAS, with the additional benefit of producing biogas. However, WAS from P&P mills contains complex lignocellulosic compounds, which inhibit the digestion of the substrate. Considering the slow rates of substrate removal (0.3 to 11 gCOD/gVSS.d) (Rajagopal *et al.* 2013) and slow bacterial growth rates (0.02 to 0.04 gVSS/gCODremoved) (Mermillod *et al.* 1992) inherent in the anaerobic processes, it requires high-volume reactors operating with a high retention time, turning this option economically unfavorable (Meyer and Edwards 2014).

Pretreatment technologies maximize the soluble fraction of the sludge organic matter prior to applying anaerobic digestion. Different methods have been investigated based on biological, chemical, thermal, and mechanical processes (Elliot and Mahmood 2007; Meyer and Edwards 2014; Li *et al.* 2019). Defined as "methods of sludge disintegration", pretreatment leads to a desired soluble chemical oxygen demand and/or protein increase in the liquid phase, resulting in an easier conversion of organic matter to methane. Promising results related to the increase of biogas production, organic matter removal, and reduction of the retention time required for the anaerobic digestion have been reported (Elliot and Mahmood 2007; Meyer and Edwards 2014).

Thermal, thermal-alkaline, and mechanical sludge pretreatments for anaerobic digestion are the most studied methods (Elliot and Mahmood 2007; Meyer and Edwards 2014; Li *et al.* 2019). The results of research are promising, and a considerable increase in methane production has been observed using WAS from P&P mills, e.g., 110 mL/mgCOD for thermal-alkaline and 115 mL/mgCOD for thermal pretreatments, compared with 30 mL/mgCOD for raw sludge (Wood *et al*. 2009, 2010), and more than 100% increase after mechanical pretreatment (Elliot and Mahmood 2012).

For P&P mill sludge, thermal pretreatment conditions include temperatures between 70 and 190 °C (Bayr *et al*. 2013; Huang 2015) and retention time from 10 to 60 min (Wood *et al*. 2009; Wood *et al*. 2010; Bayr *et al*. 2013). Usually, longer retention times are related to lower temperatures. Thermal-alkaline pretreatment was tested at pH 12 and 140 °C for 60 min (Wood *et al*. 2009, 2010). Mechanical methods included mechanical shearing (1500 rpm in alkaline conditions for 30 min), sonication (20 kHz), and high-pressure homogenization of 83 MPa in alkaline conditions (Elliot and Mahmood 2012). Commercial pretreatment plants are available, based on thermal hydrolysis process, e.g., Cambi® (Norway) and Lystek® (Canada), both suitable for anaerobic digestion optimization by disintegration of microbial cell walls and hydrolyses of complex macromolecules into simpler compounds from several biosolids. Nevertheless, there are still gaps in the knowledge, such as the effects of pH on the solubilization of organic matter at different temperatures and the effects of the retention time during the mechanical disintegration.

The effects of pretreatment are still unclear, considering the large discrepancy between the results reported in the literature, even when the same pretreatment types were compared, e.g., 60 $mLCH_4/gVS$ (Kinnunen *et al*. 2015) to 182 $mLCH_4/gVS$ (Zhang *et al*. 2016) for thermal pretreatment. Most studies have been limited to investigating the increase in biogas production through biochemical methane potential (BMP) tests, without verifying the real effects of pretreatment on sludge solubilization (for example, COD and nutrient solubilization before and after the pretreatment tests). Considering that the increase in biogas yield occurs due to the previous solubilization of the organic matter caused by the pretreatment, as evidenced in several studies (Wood *et al*. 2009, 2010; Bayr *et al*. 2013; Karlsson *et al*. 2015; Kinnunen *et al*. 2015; Veluchamy *et al*. 2017, 2018), a deeper understanding of the effects of pretreatment is needed for the optimization of the anaerobic process.

Although experimental BMP tests are widely applied for determining methane yield and anaerobic digestion configurations, there are some methodologies used to save costs and time from this process by using the theoretical biochemical methane potential (BMPth) of a substrate considering its organic composition. Methodologies based on the elemental composition for the determination of theoretical production fit better with the experimental results and behavior (Nielfa *et al*. 2015). BMPth is widely recognized in order to give an indication of the maximum methane production expected from a specific waste. A review on the methods for determination of biomethane potential mentioned that theoretical studies are significant and constitute an interesting option, especially in cases where access to laboratory facilities is limited (Jingura and Kamuso 2017). For P&P sludge, the methane yield ranges from 40 to 60% of the theoretical potential (Rodriguez-Chiang and Dahl 2015).

The objective of this research was to present and evaluate different thermal, thermal-alkaline, and mechanical pretreatments, in order to find the best condition for organic matter and nutrient solubilization and theoretical methane production for WAS generated in a Brazilian *Eucalyptus* bleached kraft pulp mill.

## 2 EXPERIMENTAL

### 2.1 Sampling

The WAS samples were collected from an ETP of a bleached kraft pulp mill located in Southeast Brazil. The mill uses *Eucalyptus* sp. as raw material for pulp production (approximately 1 Mt of ADT/year). The effluent treatment process consists of a primary clarifier followed by a conventional activated sludge plant. Approximately 15 kg of WAS/ADT of pulp (dry basis) is generated. Approximately 300 L of WAS were collected from the return line of the secondary clarifier and stored according the sampling and samples preservation methods (USEPA 2013): 50-L plastic flasks, at temperatures below 4 °C, with additional samples placed into acidified glass flasks ($H_2SO_4$ to pH < 2) for chemical oxygen demand, nitrogen, and phosphorus analyses.

### 2.2 Pretreatment tests

Figure 4 summarizes the experimental design of the pretreatment tests. In all, 16 different thermal, thermal-alkaline, and mechanical pretreatment operating conditions were tested in duplicate, resulting in 32 tests. The tested conditions were chosen based on published results for pretreatment prior to anaerobic digestion tests using WAS from a municipal wastewater treatment plant (Valo *et al*. 2004) and WAS from pulp and paper ETPs (Wood *et al*. 2009; Elliot and Mahmood 2012; Bayr *et al*. 2013).

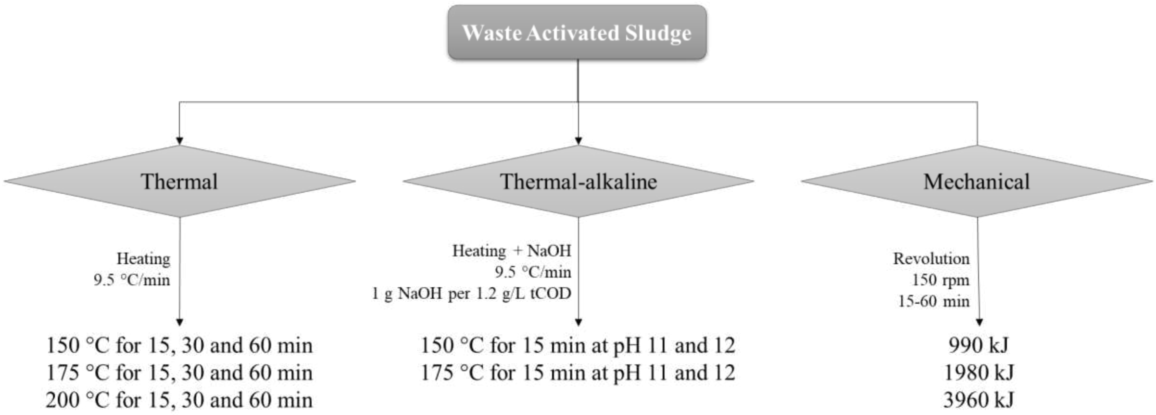


**Figure 4**. Experimental setup for pulp mill waste activated sludge pretreatment tests

Thermal (T) and thermal-alkaline (TA) pretreatment 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. The reactor is made of stainless steel and designed to withstand high temperatures and pressures. For each pretreatment test, 4 L of WAS 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. Heating rate was measured in 9.5 °C per minute. Retention time was measured from the moment that the desired temperature was reached.

For thermal-alkaline pretreatment, pH adjustment was carried out by using sodium hydroxide (NaOH), a pH probe, and a shaker table. The experiment required 5.5 g to achieve pH 11 and 6.2 g to achieve pH 12, resulting in a relation of approximately 1 g NaOH per 1.2 g/L tCOD. The pH adjustment was performed immediately before the pretreatment tests started, in order to verify if the pH increase contributes to a reduction of the required retention time.

Mechanical (M) pretreatment was carried out using a centrifugal mill (REGMED Jokro MJK-6, São Paulo, Brazil), according to NBR 14.346 (NBR 14.346 1999), using 16 g (dry basis) of WAS previously disintegrated. It was tested under three conditions in terms of energy input: 990 kJ (150 rpm for 15 min), 1980 kJ (150 rpm for 30 min) and 3960 kJ (150 rpm for 60 min). Due to the equipment characteristics, rotation could not be changed, and the influence of stirring speed was not evaluated.

## 2.3 Analytical methods

Chemical characterization of WAS, performed before and after the pretreatment tests, included the following parameters: total chemical oxygen demand (tCOD) and soluble chemical oxygen demand (sCOD) – method 5220-D (APHA/AWWA 2012); biochemical oxygen demand ($BOD_5$) – method 5210 (APHA/AWWA 2012); total phosphorus (P) – method 4500-P (APHA/AWWA 2012); total *Kjeldahl* nitrogen (TKN) – method 1687 (EPA 2001a); ammonia-nitrogen ($NH_3$-N) – method 1689 (EPA 2001b); volatile solids (VS) – method 2540 (APHA/AWWA 2012); and elemental composition (C, H, N, O) – according to the analyst's manual of TruSpec Micro CHN and TruSpec O (LECO, St. Joseph, MI , USA). For sCOD it was used filters with 0.45 µm pore size. All the analysis was performed in triplicate and the results are expressed as the mean ± standard deviation.

### 2.4 WAS Disintegration and Theoretical BMP

Sludge floc structure was observed before and after pretreatment tests using a digital microscope (RoHS®, Nanjing, China).

The empirical biomass formula (CaHbOcNd) was determined according to Rittmann and McCarty (2012). BMPth was calculated using the stoichiometric equation (Eq. 1) based on the atomic composition of the WAS using the Buswell equation (Eq. 2).

$$C_aH_bO_cN_d + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4}\right) H_2O \rightarrow$$
$$\left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8}\right) CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8}\right) CO_2 + dNH_3 \text{ (Eq. 1)}$$

$$BMPth\ (mLCH_4) = 22.4 * \left[\frac{\left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8}\right)}{12a + b + 16c + 14d}\right] * 1000 \text{ (Eq. 2)}$$

### 2.5 Statistical analysis

Data analysis was performed using the Ryan-Joiner test for verifying whether the results were normally distributed. Statistical significance was examined by analysis of variance (ANOVA) and *post hoc* Tukey test to evaluate the difference of the averages for data with normal distribution. The Kruskal-Wallis method was used when the results did not follow a normal distribution, and the *post hoc* Dunn test was employed to evaluate the difference of the averages. The probability level of $p < 0.05$ was considered significant. Minitab 17.1.0 (MINITAB®, 2016, State College, PA, USA) and XLSTAT 2020.4.1 (Addinsoft, 2020 – New

York, USA) software were used in order to perform the statistical tests, and SigmaPlot 11.0 (Systat Software, 2008, Chicago, IL, USA) was used to produce the graphs.

## 3 RESULTS AND DISCUSSION

### 3.1 Organic Matter Solubilization and Floc Disintegration

Total COD raised from 7.55 g/L (raw sludge) to 8.43 to 9.12 g/L (M pretreatment), to 8.81 to 11.04 g/L (T pretreatment), and to 10.85 to 12.07 g/L (TA pretreatment), an increase of 12 to 60% (Figure 5). The increase in sCOD was even greater, from 1.11 g/L (raw sludge) to 7.30 to 7.50 g/L (M pretreatment), to 7.33 to 10.73 g/L (T pretreatment) and to 9.21 to 11.46 g/L (TA pretreatment), an increase of 656 to 1,030%. The maximum tCOD (12.07 g/L) and sCOD (11.46 g/L) values from these tests were obtained with the TA conditions of 175 °C for 15 min at pH 12.

Statistically, the best results for tCOD were achieved with the TA conditions of 175 °C for 15 min at pH 12 (12.07 g/L), 150 °C for 15 min at pH 12 (11.35 g/L), and 175 °C for 15 min at pH 11 (11.09 g/L) (see the Appendix B, Tables S1 and S2). For sCOD, the best results were with the TA conditions of 175 °C for 15 min at pH 12 (11.46 g/L) and with the T conditions of 175 °C for 30 min (10.73 g/L). For both tCOD and sCOD, the lowest solubilization was shown with the M tests, significantly lower than the TA results.

$BOD_5$ also sharply rose from 0.57 g/L (raw sludge) to 2.43-2.60 g/L (M pretreatment), to 2.34-2.77 g/L (T pretreatment) and to 2.77-2.94 g/L (TA pretreatment), an increase of 427-516%. The maximum $BOD_5$ (2.94 g/L) was obtained from the TA conditions of 175 °C for 15 min at pH 11. Mechanical pretreatment conditions showed a significantly lower $BOD_5$ solubilization when compared with the TA tests (see the Appendix B, Tables S1 and S2).

Pretreatment increased the organic matter content and significantly increased sCOD/tCOD and $BOD_5$/tCOD ratios. An initial sCOD/tCOD ratio of 0.15 was achieved for the raw sludge, with a final ratio above 0.80 after all tested pretreatment approaches. For BOD5/tCOD, the initial ratio of 0.08 was raised to 0.24-0.30 after the sludge pretreatments. These results indicate that there was an extensive hydrolysis of the particulate organic matter in addition to an increase in the biodegradable content of the organic matter as a result of the sludge pretreatment application (see the Appendix B, Figure S1).

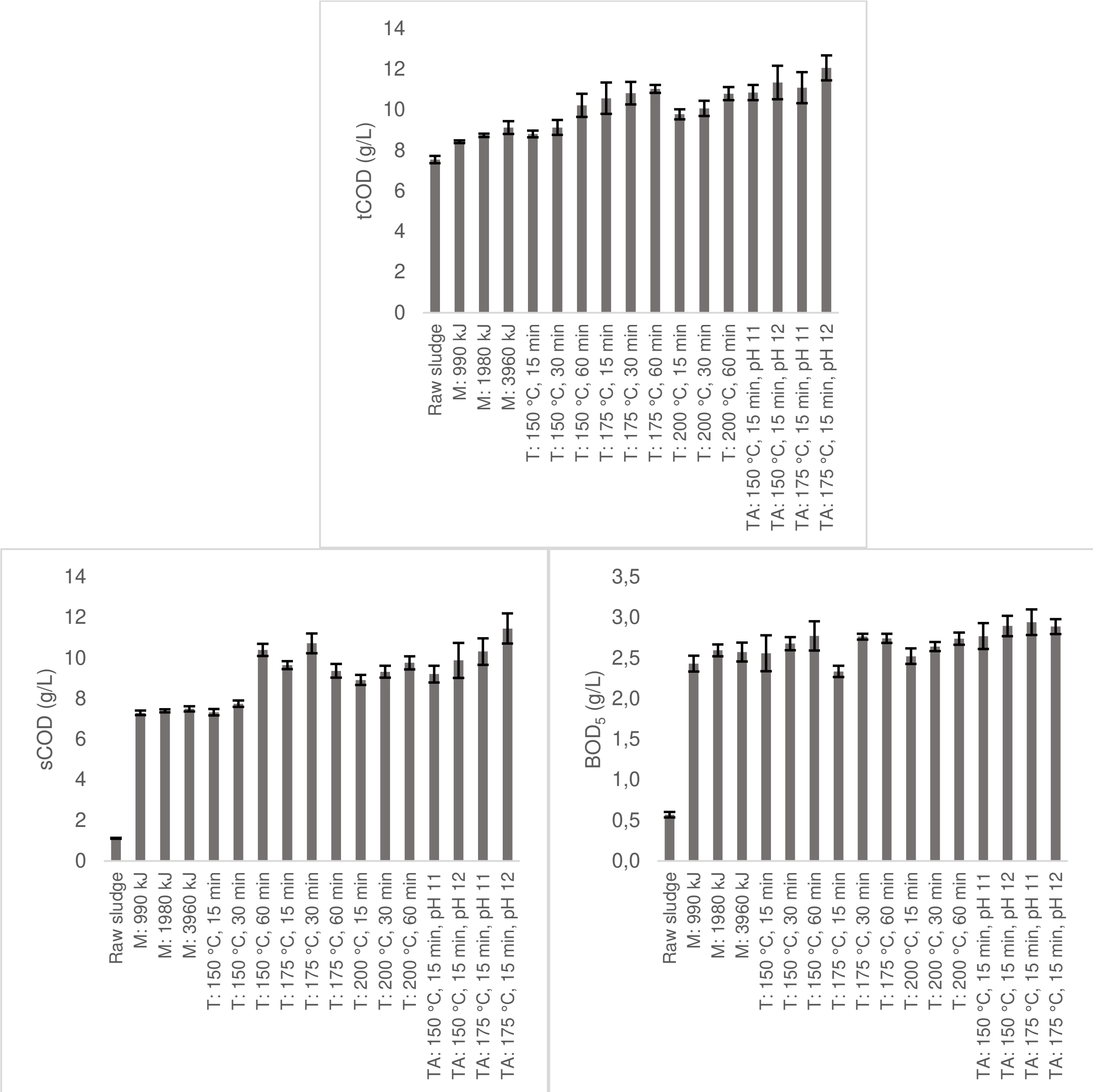


**Figure 5.** Total chemical oxygen demand (tCOD), soluble chemical oxygen demand (sCOD) and biochemical oxygen demand ($BOD_5$) solubilization after mechanical (M), thermal (T) and thermal-alkaline (TA) pretreatment tests for kraft pulp mill waste activated sludge

Mechanical sludge pretreatment techniques help to remove small fibers that are potentially difficult to degrade in a subsequent anaerobic digester (Elliot and Mahmood 2012), but the results are always inferior to those achieved when higher temperatures or alkalinity are applied. A study where three different mechanical methods for pretreatment of P&P mill WAS were compared showed the best results for solubilization and for biogas production when mechanical homogenization was combined with WAS alkalization (Elliot and Mahmood 2012). This indicates that the use of high temperatures and alkalization are more effective to rupture the cell membranes than mechanical disintegration alone.

The present results were similar to those reported for thermal and thermal-alkaline pretreatments of pulp mill WAS (Table 4). Wood *et al*. (2009, 2010) found a 6-fold increase in sCOD concentration after T pretreatment of 170 °C for 60 min and a 7-fold increase after TA pretreatment of 140 °C for 60 min at pH 12, using WAS from a sulfite pulp mill. Bayr *et al.* (2013) achieved a 4-fold increase after 70 °C for 40 min and a 9-fold increase after 150 °C for 10 min, also using WAS from a sulfite mill. The present results are also similar to those reported for municipal sewage WAS, where the fraction of sCOD increased more than 10 times using the T pretreatment (Valo *et al.* 2004). Donoso-Bravo *et al.* (2011) and Zhang *et al.* (2016) demonstrated that temperature affects sCOD, due to the effect on the bacterial cell, leading to a sub sequential cell breakage and macromolecular destruction.

**Table 4**. Soluble chemical oxygen demand (sCOD) before and after pretreatment tests in pulp mill secondary sludge

| Pretreatment condition | sCOD (g/L) | | Increase | Reference |
|---|---|---|---|---|
| | before | after | | |
| Mechanical conditions | 1.1 | 7.3-7.5 | 7-fold | This study |
| Thermal conditions | 1.1 | 7.3-10.7 | 7-10-fold | This study |
| Thermal-alkaline conditions | 1.1 | 9.2-11.5 | 8-10-fold | This study |
| Thermal: 70 °C, 40 min | 1.0 | 4.0 | 4-fold | Bayr *et al*., 2013 |
| Thermal: 150 °C, 10 min | 1.0 | 9.0 | 9-fold | Bayr *et al*., 2013 |
| Thermal: 170 °C, 60 min | 1.4 | 8.5 | 6-fold | Wood *et al*., 2009 |
| Thermal-alkaline: 140 °C, 60 min, pH 12 | 1.4 | 9.7 | 7-fold | Wood *et al*., 2009 |
| Mechanical shear | 1.4 | 2.9 | 2-fold | Elliot & Mahmood, 2012 |

The destruction of the sludge floc was observed after the pretreatment tests by microphotography (Figure 6).

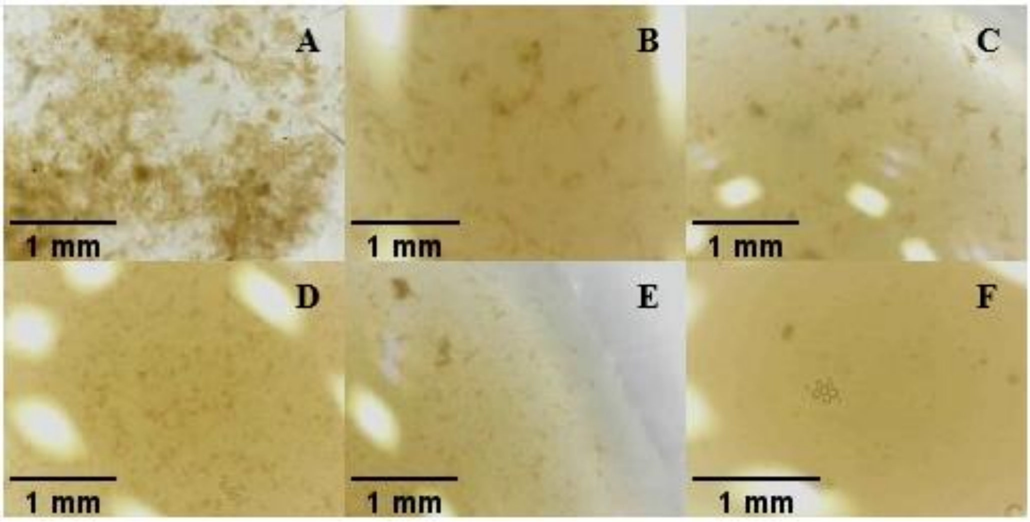


**Figure 6.** Microphotograph of waste activated sludge: raw sludge (A); after mechanical pretreatment at 9,000 revolutions (B); after thermal pretreatment at 150 °C for 15 min (C); after thermal pretreatment at 200 °C for 15 min (D); after thermal-alkaline pretreatment at 150 °C for 15 min at pH 11 (E); after thermal-alkaline pretreatment at 175 °C for 15 min at pH 12 (F).

The results showed that at either temperature, alkali addition and mechanical rotation disrupted the sludge floc structure when compared with the raw sludge sample. Most of the sludge macromolecules were degraded into small units after pretreatment, which is desirable, since these are easier for the microorganisms to decompose in order to increase the methane yield in the anaerobic digestion stage. Similar results were shown by Lin *et al*. (2009; 2010), with sludge disruption seen after the biological and alkaline tests. In both studies, the authors showed that the increase in sCOD was accompanied by the disruption of the sludge floc caused by the pretreatment applied.

A possible mechanism for improvement of biogas production in anaerobic digestion is additional COD and $BOD_5$ solubilization as a result of pretreatment, making the organic matter more available for digestion. Previous studies showed COD solubilization to be the principal mechanism for enhancing anaerobic digestibility (Wood *et al*. 2009, 2010; Bayr *et al*. 2013). A rise of 24% in methane production was observed when sCOD increased 9 times after thermal pretreatment (Bayr *et al*. 2013). It is the first step in improving biogas production and making the anaerobic technology of WAS viable for full-scale implementation in P&P mills.

### 3.2 Nutrients solubilization

Chemical tests showed that the amount of TKN in the raw sludge was 366 mg/L, but only 29 mg/L (8%) of this was in the soluble form. All pretreatment conditions improved the solubilization. The soluble form of TKN rise to 297-300 mg/L (M pretreatment), to 296-309 mg/L (T pretreatment) and to 307-310 mg/L (TA pretreatment) (Figure 7). The maximum TKN (310 mg/L) from these tests was obtained with TA conditions of 150 °C for 15 min at pH 12 and 175 °C for 15 min at pH 11.

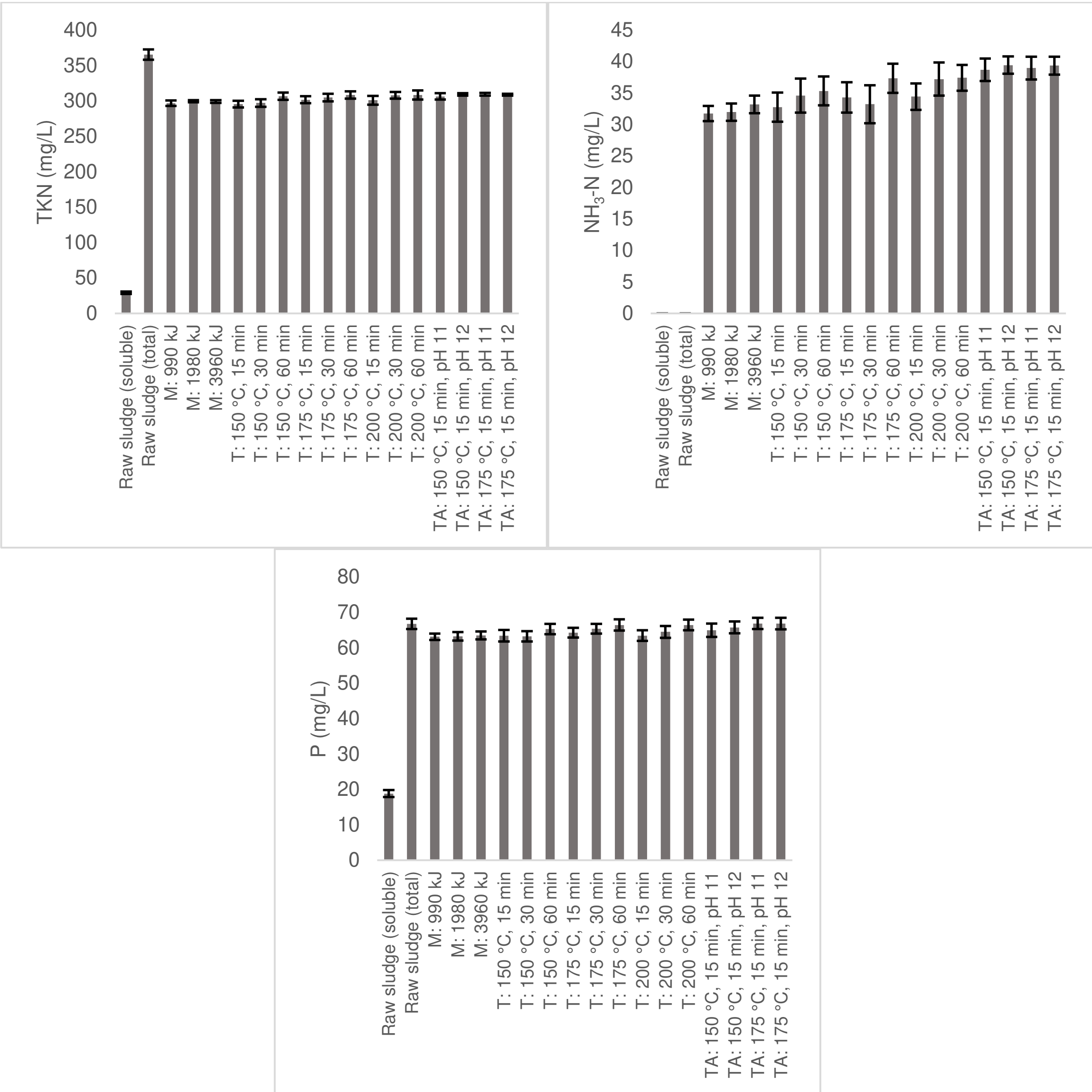


**Figure 7**. Total *Kjeldahl* nitrogen (TKN), ammonia-nitrogen ($NH_3$-N) and total phosphorus (P) solubilization after mechanical (M), thermal (T) and thermal-alkaline (TA) pretreatment tests for kraft pulp mill waste activated sludge

Mehrdadi *et al*. (2012) also showed TKN solubilization after WAS pretreatment. The authors reported increased values from 5.6% to 170.8% of TKN using ultrasonic wave irradiation, explaining that solubilizing the WAS and consequently supplying nitrogen components to the biological treatment units would accelerate the treatment process.

$NH_3$-N content was undetected in the raw sludge but showed a concentration of 32-33 mg/L after the M pretreatment, 33-37 mg/L after the T pretreatment and 39 mg/L after the TA pretreatment. The increase in $NH_3$-N can be explained by the protein decomposition, as already demonstrated by Lin *et al*. (2009, 2010) after alkaline and biological pretreatments using P&P mill WAS.

The reported results demonstrated an $NH_3$-N increase after pretreatment tests for pulp mill WAS ranging from 2-fold (Lin *et al*. 2009) to 11-fold (Lin *et al.* 2010) (Table 5). Zhang *et al*. (2016) also highlighted the quick release of ammonia with temperatures above 100 °C, which can be explained by the protein conversion to peptides and volatile fatty acids of smaller molecular weight, and also by the ammonia production through the cleavage of amine functional groups of ammonia acids (-$NH_2$), as well as from the destruction of the peptide bonds (-NH-CO-).

**Table 5**. Ammonia-nitrogen ($NH_3$-N) before and after pretreatment tests in pulp mill waste activated sludge

| Pretreatment | $NH_3$-N (mg/L) | | Increase | Reference |
|---|---|---|---|---|
| | before | after | | |
| Mechanical conditions | un[(1)] | 32-33 | - | This study |
| Thermal conditions | un[(1)] | 33-37 | - | This study |
| Thermal-alkaline conditions | un[(1)] | 39 | - | This study |
| Alkaline: 4 gNaOH/100 g TS sludge | 0.85[(2)] | 1.24[(2)] | 2-fold | Lin *et al*. (2009) |
| Alkaline: 8 gNaOH/100 g TS sludge | 0.85[(2)] | 1.38[(2)] | 2-fold | Lin *et al*. (2009) |
| Alkaline: 16 gNaOH/100 g TS sludge | 0.85[(2)] | 1.24[(2)] | 2-fold | Lin *et al*. (2009) |
| Mechanical shear: 1500 rpm, pH 12 | 47 | 93 | 2-fold | Elliot and Mahmood (2012) |
| Sonication: 20 kHz | 47 | 205 | 4-fold | Elliot and Mahmood (2012) |
| High-pressure homogenization: 83000 kPa in alkaline conditions | 47 | 538 | 11-fold | Elliot and Mahmood (2012) |

[(1)]undetected, [(2)]g/L

The decomposition of organic matter releases nitrogen compounds, mainly those containing proteins, amino acids and urea (Suschka and Grübel 2014). Nitrogen is essential for the growth and maintenance of microorganisms, but its inhibitive effect on methane production can be observed at high concentrations. Despite the increase in the $NH_3$-N concentration, it is still below the inhibitive range. The inhibitory effects of ammonia have been related to the methanogenesis phase in anaerobic digestion (Cali *et al*. 2005; Yan *et al*. 2021). Yan *et al*. (2021) cites some problems related to the application of thermal strategies for sludge hydrolysis, including high residual ammonia. Despite this, a critical threshold concentration was reported to range from 1,500 to 7,000 mg/L (Rajagopal *et al*. 2013).

Nutrient solubilization and nutrient recycling capacity were demonstrated by Sun *et al*. (2013) after thermal treatment in sewage sludge (180-240 °C for 30-90 min). The authors showed that 40-70% of the nitrogen and 10-15% of the phosphorus in sewage sludge could be dissolved into the liquid phase, suggesting that temperature is effective for solubilizing the sludge. The results of the present research suggest that pH also has an important role in the solubilization, along with temperature.

WAS nutrient solubilization is important since anaerobic digestion consists of biochemical processes carried out by essential microorganisms. Nutrients are essential for the success of microorganism growth and maintenance. Despite the large amount of nitrogen and phosphorus compounds in WAS, the major parts are in insoluble forms, forcing the hydrolyzation by the microorganisms and limiting the biological processes. Through the previous solubilization of nutrients caused by pretreatment, there was an improvement in the anaerobic digestion stage due to the acceleration of the hydrolyze phase.

### 3.3 Theoretical Biochemical Methane Potential

Table 6 presents the results obtained for the C/N ratio, VS content, empirical formula and theoretical biochemical methane potential. Improvements in the C/N ratio, VS and BMPth were shown after all pretreatments tests as a result of sludge solubilization.

**Table 6.** Carbon/Nitrogen (C/N) ratio, volatile solids (VS), empirical formula and theoretical biochemical methane potential (BMPth) for raw and pretreated kraft pulp mill waste activated sludge

| Pretreatment | C/N | VS (g/g) | Empirical formula | BMPth (mLCH$_4$/gVS) |
|---|---|---|---|---|
| Untreated | 6 | 0.35 | $C_7H_{13}O_9N$ | 211 |
| M: 990 kJ | 8 | 0.37 | $C_9H_{14}O_8N$ | 333 |
| M: 1980 kJ | 8 | 0.38 | $C_9H_{14}O_8N$ | 333 |
| M: 3960 kJ | 8 | 0.37 | $C_9H_{14}O_8N$ | 343 |
| T: 150 °C, 15 min | 8 | 0.38 | $C_9H_{14}O_8N$ | 314 |
| T: 150 °C, 30 min | 8 | 0.39 | $C_9H_{14}O_8N$ | 345 |
| T: 150 °C, 60 min | 8 | 0.40 | $C_9H_{14}O_8N$ | 355 |
| T: 175 °C, 15 min | 8 | 0.38 | $C_9H_{13}O_7N$ | 346 |
| T: 175 °C, 30 min | 8 | 0.41 | $C_9H_{14}O_7N$ | 359 |
| T: 175 °C, 60 min | 8 | 0.41 | $C_9H_{14}O_7N$ | 360 |
| T: 200 °C, 15 min | 7 | 0.38 | $C_8H_{12}O_7N$ | 344 |
| T: 200 °C, 30 min | 8 | 0.40 | $C_9H_{14}O_8N$ | 354 |
| T: 200 °C, 60 min | 8 | 0.39 | $C_9H_{14}O_7N$ | 360 |
| TA: 150 °C, 15 min, pH 11 | 9 | 0.41 | $C_{10}H_{16}O_8N$ | 373 |
| TA: 150 °C, 15 min, pH 12 | 8 | 0.42 | $C_{10}H_{14}O_8N$ | 373 |
| TA: 175 °C, 15 min, pH 11 | 8 | 0.42 | $C_9H_{12}O_6N$ | 378 |
| TA: 175 °C, 15 min, pH 12 | 8 | 0.43 | $C_9H_{14}O_7N$ | 376 |

The C/N ratio improved from 6 in the raw sludge to 7-9 after pretreatment tests, with better results under the TA conditions. Despite improvements, the C/N ratio remained below the optimal value indicated for anaerobic digestion, which is between 20 and 30 (Banks and Heaven 2013). A better C/N ratio may be achieved with co-digestion. Nevertheless, there are no reports of inhibition related to the unbalanced C/N ratio. Park *et al.* (2012) did not achieve an increase in the C/N ratio after different alkaline and ultrasonic pretreatments using pulp mill WAS; however, this did not affect the increase in methane production, even with an initial C/N ratio around 10.

Elemental composition was changed as the VS contend changed. The values raised from 0.35 gVS/g (raw sludge) to 0.37-0.43 gVS/g after pretreatment tests. An increase on the VS values was accompanied by an increase in C in the empirical formula as a result of cells walls rupture and organic matter released. Liew *et al*. (2022) presented some examples about the importance of VS content for biogas production; according to their review, higher contents of VS result in more produced energy in the form of biogas.

BMPth increased in all the pretreatments tested by at least 100 mL$CH_4$/gVS. The results ranged from 211 mL$CH_4$/gVS (raw sludge) to 333-343 mL$CH_4$/gVS (M pretreatment), to 314-360 mL$CH_4$/gVS (T pretreatment, and to 373-378 mL$CH_4$/gVS (TA pretreatment), an increase of 149-179%. The maximum BMPth was obtained with the TA conditions, all exceeding 373 mL$CH_4$/gVS. In contrast, the minimum values were obtained with the T condition of 150 °C for 15 min (314 mL$CH_4$/gVS) and with all the M tests (333-343 mL$CH_4$/gVS).

In practice, no reaction goes to full completion, and it is impossible to have total breakdown of cellulosic materials. Although the results only give a maximum biogas production potential and overestimate the real biogas yields, the results seem to be very promising when comparing the BMPth values with literature (Table 7). The application of a limiting factor ($f$ = 80%) was proposed to give more reliable results and eliminate the discrepancy between hypothetical and real biogas amount when Buswell equation was applied (Achinas and Euverink 2016). Applying the $f$ factor (adjusted BMPth), the results of this research were still higher than the experimental values determined by other authors (Bayr *et al*. 2013; Kinnunen *et al*. 2015).

The BMP results provide an indication of the biodegradability of a substrate and its potential for producing methane via anaerobic digestion. Such information allows a direct assessment of the biogas yields achieved by the anaerobic process. From an economic perspective for P&P mills, these results show that methane can be obtained from WAS and that the investment in anaerobic digestion technology may provide energy (biogas) and also fertilizer (digestate) that can be applied in the forestry field, reinforcing the production of raw material for the industry. In comparison, Meyer *et al*. (2020) explained that anaerobic digestion system requires a lower capital cost than other techniques, citing that it could cost at least 3 times less than incineration.

**Table 7**. Biochemical Methane Potential (BMP) for pulp mill waste activated sludge, in $mLCH_4/gVS$

| Pretreatment | Theoretical BMPth | Adjusted BMPth | Experimental BMP | Reference |
|---|---|---|---|---|
| Raw sludge | 211 | 169 | - | This study |
| Mechanical conditions | 333-343 | 266-274 | - | This study |
| Thermal conditions | 314-360 | 251-288 | - | This study |
| Thermal-alkaline conditions | 373-378 | 298-303 | - | This study |
| Thermal: 150 °C, 10 min | - | - | 134 | Bayr *et al*. (2013) |
| Thermal: 70 °C, 40 min | - | - | 112 | Bayr *et al*. (2013) |
| Thermal: 80-134 °C, 20-120 min | - | - | 60-124 | Kinnunen *et al*. (2015) |

One possibility to be considered is the use of heat energy, commonly in the form of high-pressure steam generated in the boilers, as the heat source for the pretreatment and anaerobic reactors, thus reducing the operating costs. The biogas produced can be burned in a combined heat and power (CHP) plant to simultaneously generate electricity and heat. Considering the possible process routes, a CHP system can also produce heat for the pretreatment and anaerobic reactors and electrical power for the ETP. This can reduce the operational costs for the pretreatment while providing power for pumps and aerators, making the ETP a self-sufficient sector in terms of energy. Another way for reducing the operating costs was presented by Jian *et al*. (2021), using black liquor (pH 12.8, 4.1 g/L of residual alkali) to replace NaOH for the pretreatment using sludge from a soda pulping mill. The authors showed that adding black liquor increased sCOD concentration and increased the amount of methane produced, demonstrating the economic feasibility of this strategy.

## 4 CONCLUSIONS

1. Pulp mill waste activated sludge (WAS) solubilization was achieved with thermal, thermal-alkaline and mechanical pretreatments. For organic matter solubilization, the bests results were achieved with the thermal-alkaline (TA) operating conditions of 175 °C for 15 min at pH 12 for tCOD and sCOD and 175 °C for 15 min at pH 11 for $BOD_5$.

2. The TA pretreatment also showed the maximum solubilization values for nutrients, in special the operation conditions of 150 °C for 15 min at pH 12, 175 °C for 15 min at pH 11 and 175 °C for 15 min at pH 12. This showed the powerful influence of pH on the solubilization, despite the low retention time (only 15 min).

3. All pretreatments improved the potential methane production by at least 100 $mLCH_4/gVS$. The bests results were achieved with the TA operating conditions, in the range of 373-378 $mLCH_4/gVS$.

4. Considering the variables studied, pH seems to be the most important parameter in the solubilization process. In general, mechanical conditions resulted in the worst results. Thermal tests, despite the higher temperature (up to 200 °C) and greater retention time (up to 60 min), resulted in lower solubilization when compared with the thermal-alkaline processes, although there was a statistical similarity for sCOD, $BOD_5$, TKN, $NH_3$-N and P. Thermal-alkaline pretreatment showed the best values for all the evaluated parameters, with the additional advantage of requiring lower temperature (150-175 °C) and retention time (15 min).

5. Future research should include a pilot scale tests for economic evaluation of both pretreatment and anaerobic digestion processes; also, for study other variables, such as the use of other sources of alkalinity, metals solubilization and the influence of pretreatment on the volatile organic acid concentrations.

**REFERENCES**


NBR 14.346 (1999) "Pasta celulósica: Refinação em laboratório - Método Jokro," Associação Brasileira de Normas Técnicas, Brasília, Brazil.

Achinas, S., and Euverink, G. J. W. (2016). "Theoretical analysis of biogas potential prediction from agricultural waste," *Resource-Efficient Technologies* 2(3), 143-147. DOI: 10.1016/j.reffit.2016.08.001

American Public Health Association, American Water Works Association (APHA/AWWA) (2012). *Standard Methods for the Examination of Water and Wastewater*, Washington, D.C.

Banks, C. J., and Heaven, S. (2013). "Optimisation of biogas yields from anaerobic digestion by feedstock type," in: *The Biogas Handbook*, A. Wellinger, J. Murphy, and D. Baxter (eds.), Woodhead Publishing Limited, Sawston, UK.

Bayr, S., Kaparaju, P., and Rintala, J. (2013). "Screening pretreatment methods to enhance thermophilic anaerobic digestion of pulp and paper mill wastewater treatment secondary sludge," *Chem. Eng. J.* 223(1), 479-486. DOI: 10.1016/j.cej.2013.02.119

Calli, B., Mertoglu, B., Inanc, B., and Yenigun, O. (2005). "Effects of high free ammonia concentrations on the performances of anaerobic bioreactors," *Process Biochem.* 40(3-4), 1285-1292. DOI: 10.1016/j.procbio.2004.05.008

Donoso-Bravo, A., Pérez-Elvira, S., Aymerich, E., and Fdz-Polanco, F. (2011). "Assessment of the influence of thermal pre-treatment time on the macromolecular composition and anaerobic biodegradability of sewage sludge," *Bioresource Technol.* 102(2), 660-666. DOI: 10.1016/j.biortech.2010.08.035

Elliott, A., and Mahmood, T. (2005). "Survey benchmarks generation, management of solid residues," *Pulp Paper* 79(12), 49-55.

Elliott, A., and Mahmood, T. (2007). "Pretreatment technologies for advancing anaerobic digestion of pulp and paper biotreatment residues," *Water Res.* 41(19), 4273-4286. DOI: 10.1016/j.watres.2007.06.017

Elliott, A., and Mahmood, T. (2012). "Comparison of mechanical pretreatment methods for the enhancement of anaerobic digestion of pulp and paper waste activated sludge," *Water Environ Res.* 84(6), 497-505. DOI: 10.2175/106143012X13347678384602

EPA (2001a). "Total Kjeldahl nitrogen in water and biosolids by automated colorimetry with preliminary distillation/digestion," U.S. Environmental Protection Agency, Washington, D.C., USA.

EPA (2001b). "Ammonia-N in water and biosolids by ion-selective electrode potentiometry with preliminary distillation," U.S. Environmental Protection Agency, Washington, D.C., USA.

Huang, X. M. (2015). *Enhancing Anaerobic Digestion of Pulp and Paper Mill Biosludge* *using Thermal Treatment in a Bench-scale System*, Master's Thesis, University of Toronto, Toronto, Canada.

Jian, Z., Yuan-Fang, P., Wan-Li, W., Qin, W., Gong-Nan, X., Hong-Fei, L., Tian, X., and Shuang-Fei, W. (2021). "Black liquor increases methane production from excess pulp and paper industry sludge," *Chemosphere* 280. DOI: 10.1016/j.chemosphere.2021.130665

Jingura, R. M., and Kamusoko, R. (2017). "Methods for determination of biomethane potential of feedstocks: A review," *Biofuel Re.s J*. 14, 573-586. DOI: 10.18331/BRJ2017.4.2.3

Kamali, M., Gameiro, T., Costa, M. E. V., and Capela, I. (2016). "Anaerobic digestion of pulp and paper mill wastes – An overview of the developments and improvement opportunities," *Chem. Eng. J*. 298, 162-182. DOI: 10.1016/j.cej.2016.03.119

Karlsson, A., Truong, X. B., Gustavsson, J., Svensson, B. H., Nilsson, F., and Ejlertsson, J. (2011). "Anaerobic treatment of activated sludge from Swedish pulp and paper mills – biogas production potential and limitations," *Environ Technol.* 32(14), 1559-1571. DOI: 10.1080/09593330.2010.543932

Karlsson, R. (2010) *Anaerobic Digestion of Biological Sludge from the Pulp and Paper Industry*, Ph.D. Dissertation, Linköping University, Linköping, Sweden.

Kinnunen, V., Yla-Outinen, A., and Rintala, J. (2015). "Mesophilic anaerobic digestion of pulp and paper industry biosludge-long-term reactor performance and effects of thermal pretreatment," *Water Res.* 87(15), 105-111. DOI: 10.1016/j.watres.2015.08.053

Li, Y., Chen, Y., and Wu, J. (2019). "Enhancement of methane production in anaerobic digestion process: A review," *Appl. Energ*. 240, 120-137. DOI: 10.1016/j.apenergy.2019.01.243

Liew, C. S., Yunus, N. M., Chidi, B. S., Lam, M. K., Goh, P. S., Mahamad, M., Sin, J. C., Lam, S. M., Lim, J. W., and Lam, S. S. (2022). "A review on recent disposal of hazardous sewage sludge via anaerobic digestion and novel composting," *J. Hazard Mater.* 423. DOI: 10.1016/j.jhazmat.2021.126995

Lin, Y., Wang, D., and Wang, L. (2010). "Biological pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge," *Waste Manage Res*. 28(9), 800-810. DOI: 10.1177/0734242X09358734

Lin, Y., Wang, D., Wu, S., and Wang, C. (2009). "Alkali pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge," *J. Hazard Mater.* 170(1), 366-373. DOI: 10.1016/j.jhazmat.2009.04.086

Mehrdadi, N., Zahedi, A., Yasini, A. A., and Aghdam, A. M. (2012). "Solubilization of dairy waste-activated sludge by ultrasonic wave irradiation," *Pol. J. Environ. Stud.* 21(05), 1319-1325.

Mermillod, P., Habets, L. H. A., van Driel, E. F., and de Vegt, A. L. (1992). "Compact anaerobic/aerobic wastewater treatment at the Minguet & Thomas recycled paper mill in

France," *Tappi J.* 75(9), 177-180.

Meyer, T., and Edwards, E. A. (2014). "Anaerobic digestion of pulp and paper mill wastewater and sludge," *Water Res.* 65(15), 321-349. DOI: 10.1016/j.watres.2014.07.022

Mayer, F., Bhandari, R., Gath, S. A., Himanshu, H., and Stobernack, N. (2020). "Economic and environmental life cycle assessment of organic waste treatment by means of incineration and biogasification. Is source segregation of biowaste justified in Germany?," *Sci. Total Environ*. 721, 137731. DOI: 10.1016/j.scitotenv.2020.137731

Nielfa, A., Cano, R., and Fdz-Polanco, M. (2015). "Theoretical methane production generated by the co-digestion of organic fraction municipal solid waste and biological sludge," *Biotechnol. Rep.* (Amst). 5, 14-21. DOI: 10.1016/j.btre.2014.10.005

Park, N. D., Helle, S. S., and Thring, R. W. (2012). "Combined alkaline and ultrasound pre-treatment of thickened pulp mill waste activated sludge for improved anaerobic digestion," *Biomass Bioenerg*. 46, 750-756. DOI: /10.1016/j.biombioe.2012.05.014

Rajagopal, R., Massé, D. I., and Singh, G. (2013). "A critical review on inhibition of anaerobic digestion process by excess ammonia," *Bioresource Technol*. 143, 632-641. DOI: 10.1016/j.biortech.2013.06.030

Reeve, D., and Silva, C. M. (2000). "Closed cycle systems for manufacture of bleached chemical wood pulp," in: *Chemical Pulping*, J. Gullichsen, C. Fogelholm (eds.), Fapet Oy, Jyväskylä, Finland, pp. 440-473.

Rittmann, B. E., and McCarty, P. L (2012). *Environmental Biotechnology: Principles and Applications*, McGraw Hill, New York, NY, USA.

Rodriguez-Chiang, L. M., and Dahl, O. P. (2015). "Effects of inoculum to substrate ratio on the methane potential of microcrystalline cellulose production wastewater," *BioResources* 10(1), 898-911. DOI: 10.15376/biores.10.1.898-911

Sun, X. H., Sumida, H., and Yoshikawa, K. (2013). "Effects of hydrothermal process on the nutrient release of sewage sludge," *Int. J. Waste Resour*. 3(2). DOI: 10.4172/2252-5211.1000124

Suschka, J., and Grübel, K. (2014). "Nitrogen in the process of waste activated sludge anaerobic digestion," *Arch. Environ. Prot*. 40(2), 123-136. DOI: 10.2478/aep-2014-0021

USEPA (2013). *Handbook for Sampling and Sample Preservation of Water and Wastewater*, U.S. Environmental Protection Agency, Cincinnati, OH, USA.

Valo, A., Carrère, H., and Delgenès, J. P. (2004). "Thermal, chemical and thermo-chemical pre-treatment of waste activated sludge for anaerobic digestion," *J. Chem. Technol. Biot.* 79(11), 1197-1203. DOI: 10.1002/jctb.1106

Veluchamy, C., Raju, V. W., and Kalamdhad, A. S. (2018). "Electrohydrolysis pretreatment for enhanced methane production from lignocellulose waste pulp and paper mill sludge and its kinetics," *Bioresource Technol*. 252, 52-58. DOI: 10.1016/j.biortech.2017.12.093

Veluchamy, C., Raju, V. W., and Kalamdhad, A. S. (2017). "Prerequisite – An electrohydrolysis pretreatment for anaerobic digestion of lignocellulose waste material," *Bioresource Technol*. 253, 274-280. DOI: 10.1016/j.biortech.2017.03.137

Wood, N., Tran, H. and Master, E. (2010). "Improving anaerobic conversion of pulp mill secondary sludge to biogas by pretreatment," *Tappi J.* June, 16-21.

Wood, N., Tran, H., and Master, E. (2009). "Pretreatment of pulp mill secondary sludge for high-rate anaerobic conversion to biogas," *Bioresource Technol.* 100(23), 5729-5735. DOI: 10.1016/j.biortech.2009.06.062

Yan, W., Xu, H., Lu, D., and Zhou, Y. (2021). "Effects of sludge thermal hydrolysis pretreatment on anaerobic digestion and downstream processes: mechanism, challenges and solutions," *Bioresource Technol.* (in press). DOI: 10.1016/j.biortech.2021.126248

Zhang, J., Wang, S., Lang, S., Xian, P., and Xie, T. (2016). "Kinetics of combined thermal pretreatment and anaerobic digestion of waste activated sludge from sugar and pulp industry," *Chem. Eng. J.* 295(1), 131-138. DOI: 10.1016/j.cej.2016.03.028

# CHAPTER 3

# METHANE PRODUCTION FROM MESOPHILIC ANAEROBIC DIGESTION OF WASTE ACTIVATED SLUDGE FROM A BRAZILIAN BLEACHED KRAFT PULP MILL AFTER PRETREATMENT

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## Abstract

Large volumes of waste activated sludge (WAS) are generated in biological wastewater treatment processes in pulp and paper mills. Great management efforts and high costs for treatment, transport and disposal are required, which result in the necessity for more sustainable methods of WAS management and energy recovery. This paper aims to evaluate the potential of methane production from the WAS of a bleached kraft pulp mill. Thermal and thermal-alkaline pretreatment techniques were applied for WAS solubilization prior to the biochemical methane potential (BMP) tests in order to estimate methane production. These pretreatments resulted in a high solubilization of sludge, mainly of the organic matter content. After 30 days of testing, cumulative methane production increased from 90 mL $CH_4$/gVS (raw sludge) to 181-194 mL $CH_4$/gVS with thermally pretreated samples, and up to 203-204 mL $CH_4$/gVS with samples which were pretreated using the thermo-alkaline technique. The pretreatment conditions of 175 °C for 15 min at pH 11 were sufficient to achieve both a high solubilization of WAS and a high methane production. The benefits of solubilization on the hydrolysis step were clear, since higher levels of soluble organic matter can be immediately converted by the anaerobic microorganisms. The results showed that pretreatment could significantly enhance the anaerobic digestion of kraft pulp mill WAS, making this an attractive new option for sludge management in this sector.


**Keywords**: anaerobic digestion; methane yield; pretreatment; pulp and paper mill; secondary sludge.

## 1 INTRODUCTION AND BACKGROUND

A large volume of wastewater is generated by biological effluent treatment processes in pulp and paper (P&P) mills. Activated sludge (AS) technology is the most common process used in this treatment, resulting in a huge amount of waste activated sludge (WAS) which is composed mainly of microbial biomass, lignin and chemical residuals from the wood pulping process. Traditionally, WAS is mixed with primary sludge, thickened, dewatered and disposed of in landfills, or simply incinerated [1]. In Brazil, landfilling is the most common technique for final disposal of WAS, although this has several drawbacks: landfill maintenance, high financial costs, a shortage of sites and greenhouse gas emission [2,3].

Anaerobic digestion (AD) of sludge is an attractive process due to its capability for reducing mass and volume and recovering energy. Some benefits are the stabilization and disinfection of sludge and the recovery of energy in the form of methane [4]. Other benefits, described by Karlsson *et al.* [5], include the release of nutrients into the liquid and reject water, which can be recirculated to the AS reactor, thereby reducing the need for commercial nitrogen and phosphorus to feed the bacteria.

However, AD technology has not been established in P&P mills for sludge treatment because of the low methane production, e.g., 47 $mLCH_4/gVS$ after 30 days of thermophilic anaerobic digestion tests using WAS from a Brazilian eucalyptus bleached kraft pulp mill [6]. The low methane yield of P&P mill WAS can be attributed to the fact that the sludge is already subjected to partial degradation during the AS process [1], and also to the presence of toxic chemicals [7]. Also, some limiting factors are generally associated with the hydrolysis stage [8]. Several options aiming to improve the AD process in P&P mills have been reviewed, and sludge pretreatment seems to be the most promising technology [7,9,10,11].

WAS conversion to methane is a multistep process, with at least four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Sludge pretreatment is designed to accelerate the hydrolysis stage, i.e., the rate-limiting step in methane production from P&P mill WAS [9]. Pretreatment causes the lysis of the sludge cells and produces solubilized species to increase the production rate and yield of biogas due to the transfer of organic matter from the sludge flocs to the aqueous phase [7,12,13].

Thermal and thermal-alkaline pretreatments prior to AD are potential solutions for P&P mill sludge management. The methane yield increased more than 200% after thermal (170 °C, 60 min) and thermal-alkaline (140 °C, 60 min, pH 12) pretreatments using WAS from a kraft pulp mill in batch assays [14]. Therefore, a feasible methodology for estimating and evaluating the effectiveness of the pretreatment becomes necessary. To the best of our knowledge, there is no previous study testing pretreatment for sludge solubilization with the objective of enhancing the AD process using WAS from a Brazilian eucalyptus kraft pulp mill, and this lack acts as a deterrent against the implementation of such technology in Brazilian mills.

In this study, methane production with both pretreated and raw (non-pretreated) WAS collected from a Brazilian eucalyptus bleached kraft pulp mill was estimated through biochemical methane potential (BMP) tests. The effects of previous solubilization caused by thermal and thermal-alkaline pretreatments on methane production were evaluated in bath assays at 35 °C that simulate a semi-solid anaerobic digestion state.

## 2 MATERIALS AND METHODS

### 2.1 Substrate and Inoculum

WAS samples were collected from the return line of the secondary clarifier at the activated sludge effluent treatment plant of a bleached kraft pulp mill located in southeastern Brazil. Eucalyptus sp. was used as the raw material for pulp production of approximately 1 Mt/year of ADT. The mill generates approximately 15 kg/ADT of WAS (dry basis).

The inoculum was collected from a mesophilic upflow anaerobic sludge blanket (UASB) reactor fed with sewage at the Center for Research and Training in Sanitation (CePTS), UFMG/Copasa (Arrudas Wastewater Treatment Plant, Belo Horizonte, Minas Gerais state, Brazil). It was centrifugated at 4500 rpm for 10 minutes and incubated under mesophilic conditions of 35±1 °C and stirring of 120 rpm for 7 days, in order to achieve biomass adaptation. The chemical composition of this inoculum included: 17.4% total solids, 10.34% volatile solids, 1805 mg/L of soluble chemical oxygen demand and pH of 7.6.

### 2.2 Material Characterization

Chemical characterization of the WAS included the following parameters: total chemical oxygen demand (tCOD) and soluble chemical oxygen demand (sCOD) – method 5220-D [15]; total phosphorus (P) – method 4500-P [15]; total *Kjeldahl* nitrogen (TKN) – method 1687 [16]; ammonia-nitrogen ($NH_3$-N) – method 1689 [17]; total solids (TS) and volatile solids (VS) – method 2540 B-F [15]; elemental composition (C, H, N, O) – according to the analyst's manual for TruSpec Micro CHN, TruSpec O and TruSpec S (LECO, Michigan, USA); cellulose and hemicellulose – method T 249 cm-85 [18]; and Klason lignin – method T 222 om-11 [19]. For sCOD it was used filters with 0.45 µm pore size. All the analysis was performed in triplicate and the results are expressed as the mean ± standard deviation.

The empirical biomass formula (CaHbOcNd) was determined according to Rittmann and McCarty [20]. Theoretical biochemical methane potential (BMPth) was determined using the stoichiometric equation (Eq. 1), based on the atomic composition of the WAS, using the Buswell equation (Eq. 2).

$$C_aH_bO_cN_d + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4}\right) H_2O \rightarrow$$
$$\left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8}\right) CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8}\right) CO_2 + dNH_3 \text{ (Eq. 1)}$$

$$BMP_{th} = 22.4 * \left[\frac{\left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8}\right)}{12a + b + 16c + 14d}\right] * 1000 \text{ (Eq. 2)}$$

## 2.3 Pretreatment Tests

Four pretreatments were chosen based on the best results related to the solubilization of organic matter between sixteen previously tested operational parameters (data not shown).

The pretreatment conditions are summarized in Table 8. Thermal and thermal-alkaline pretreatments were tested under two different conditions each, using 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 WAS were used, and the headspace was flushed with nitrogen gas to exclude oxygen and prevent any oxidation of the organic compounds after loading the sludge samples.

**Table 8**. Operational parameters for pretreatment of kraft pulp mill waste activated sludge

| Abbreviation | Pretreatment | Conditions |
|---|---|---|
| Raw | None | Raw sludge (control) |
| The-01 | Thermal | 175 °C, 30 min |
| The-02 | Thermal | 175 °C, 60 min |
| TheAlk-01 | Thermal-alkaline | 175 °C, 15 min, pH 11 |
| TheAlk-02 | Thermal-alkaline | 175 °C, 15 min, pH 12 |

For thermal-alkaline pretreatment, pH adjustment was carried out immediately before the pretreatment tests started by using sodium hydroxide (NaOH), a pH probe and a shaker table. It was necessary to use 5.5 g to achieve pH 11 (1.375 g NaOH per L of sludge) and 6.2 g to achieve pH 12 (1.55 g NaOH per L of sludge).

**2.4 BMP Assays**

Biochemical methane potential (BMP) assays were performed according to the methodologies proposed by Angelidaki *et al*. [21] and Holliger *et al*. [22]. These BMP assays were carried out in 120 mL serum bottles with 60 mL of headspace, in duplicate plus a blank one. The blank served as a control test (without substrate) to verify the methanogenic activity of the inoculum. It was considered a semi-solid anaerobic digestion state with 12% TS in each serum bottle.

The initial food-to-inoculum (F/I) ratio was fixed at 1 $gVS_{substrate}/gVS_{inoculum}$, as previously determined by Lopes [23]. Micro- and macro-nutrient solutions, prepared in sodium bicarbonate (buffer) according to the methodology described by Angelidaki *et al*. [21], were added prior to closing the serum bottles, in order to adjust the COD:N:P relation to 350:5:1 [24]. The initial pH was adjusted to 9.0 using NaOH (1.0 M) in order to avoid interference in the methane production from the initial pH variation.

In all, 15 BMP assays was prepared, including duplicates and controls. The bottles of these BMP assays were closed with butyl rubber stoppers and aluminum seal crimp caps, flushed with $N_2$ for about 5 min (purge) to ensure an anaerobic condition and incubated at 35±1 °C and 120 rpm in a TE-421 orbital shaker incubator (Tecnal, Sao Paulo, Brazil). Methane production was monitored every 12 hours until the methane production rate decreased. Subsequently, the monitoring was performed daily until stabilized.

Monitoring was carried out manually, including the measurement of the pressure generated by the biogas using the PM–9100HA Manometer (Lutron Electronic, Pennsylvania, USA). Each biogas sample was collected with a syringe and injected into a Shimadzu® GC-2014 gas chromatograph (Shimadzu Corp., Kyoto, Japan), equipped with a thermal conductivity detector – TCD, using $N_2$ as the carrier gas for estimating the volume of methane produced. The results were expressed in the standard conditions of temperature and pressure (275.15 K and 1 atm) as mL $CH_4$/gVS.

### 2.5 Statistical Analysis

Average final tCOD, sCOD, TKN, $NH_3$-N, P, VS, cellulose, hemicellulose and lignin were examined by analysis of variance (ANOVA) and a *post hoc* Tukey test. The probability level of $p < 0.05$ was considered significant. Minitab 17.1.0 software (MINITAB®, 2016 – Pennsylvania, USA) was used in order to perform the statistical tests, and Microsoft Excel (Microsoft Office, 2020) was used to generate the graphics.

## 3 RESULTS AND DISCUSSIONS

### 3.1 Impact of Pretreatment on the Sludge Characteristics

The purpose of the pretreatment methods applied was to solubilize the sludge and, consequently, enhance the hydrolysis step of the anaerobic digestion. Pretreatment has a potential for transforming the WAS into a more readily digestible substrate, which is beneficial for both the digestion rate and methane production.

Table 9 shows the characterization of untreated and pretreated WAS. Comparing the samples, the amounts of tCOD sCOD, TKN, $NH_3$-N and P showed a significant increase due the solubilization promoted by the pretreatment. This increase varied from 1.4 to 1.6 times for tCOD, 8 to 10 times for sCOD, 10 times for TKN and 3.5 times for P. For $NH_3$-N, an average content of 37 mg/L was found in pretreated samples, while it was undetected in the raw sludge. Similar results were reported by Bayr *et al.* [1] (thermal pretreatment) and Wood *et al.* [14] (thermal and alkaline pretreatment) for the solubilization of organic matter, and by Lin *et al.* [25] (alkaline pretreatment) and Elliot and Mahmood [13] (mechanical pretreatment) for the solubilization of nutrients. All of these authors were testing pretreatments on pulp mill WAS.

In contrast to our study, Park *et al.* [4] obtained a reduction in the tCOD content after the pretreatment, possibly due to the loss of volatile components. The authors tested alkaline and ultrasound methods for pretreatment of WAS from a bleached chemi-thermo-mechanical pulp and thermo mechanical pulp mills. In our study, all pretreatments were carried out in a closed reactor with headspace flushed with nitrogen gas to exclude oxygen and prevent any oxidation of the organic compounds. This technique avoids the loss of organic matter and, consequently, the loss of feedstock for methane production. Nevertheless, Park *et al.* [4] also found an improvement in sCOD after pretreatment, with an increase in sCOD/tCOD of 3 to 5 times. In most studies, sCOD increased after pretreatment; for example, more than 1.6 times after electrohydrolysis [26] and more than 20-fold after thermal pretreatment using kraft mill WAS [14].

**Table 9**. Characteristics of raw and pretreated waste activated sludge from a bleached kraft pulp mill

| Parameters | Sample | | | | |
|---|---|---|---|---|---|
| | **Raw** | **The-01** | **The-02** | **TheAlk-01** | **TheAlk-02** |
| tCOD (mg/L) | 7,549±173 *c* | 10,823±552 *b* | 11,037±198 *b* | 11,091±767 *b* | 12,074±615 *a* |
| sCOD (mg/L) | 1,112±22 *d* | 10,729±492 *ab* | 9,368±336 *c* | 10,321±647 *b* | 11,456±743 *a* |
| TKN (mg/L) | 29±2 *b* | 305±6 *a* | 309±5 *a* | 310±2 *a* | 309±1 *a* |
| $NH_3$-N (mg/L) | un [(1)] | 33±3 *b* | 37±2 *a* | 39±2 *a* | 39±1 *a* |
| P (mg/L) | 19±1 *b* | 65±1 *a* | 66±2 *a* | 67±2 *a* | 67±2 *a* |
| VS (g/g sample) | 0.35±0.001 *d* | 0.41±0.01 *c* | 0.43±0.006 *ab* | 0.42±0.003 *b* | 0.44±0.003 *a* |
| Cellulose (% TS) | 30.57±1.14 *a* | 32.89±2.09 *a* | 31.93±2.87 *a* | 32.87±1.67 *a* | 32.67±1.98 *a* |
| Hemicellulose (% TS) | 5.87±0.11 *a* | 2.54±0.54 *b* | 2.14±0.52 *b* | 2.39±0.18 *b* | 2.22±0.17 *b* |
| Lignin (% TS) | 21.98±2.78 *a* | 16.91±2.96 *b* | 16.18±2.22 *b* | 15.84±2.04 *b* | 14.19±2.10 *b* |
| Theoretical $CH_4$ yield (mL $CH_4$/gVS) | 211 | 359 | 360 | 378 | 376 |

tCOD: total chemical oxygen demand; sCOD: soluble chemical oxygen demand; TKN: total *Kjeldahl* nitrogen; $NH_3$-N: ammonia-nitrogen; P: phosphorus; VS: volatile solids
[(1)] undetected
Means that do not share a letter in the same line are significantly different, considering 95% confidence

Cellulose content showed a slight increase of 1.04-1.08 times in pretreated WAS. Simultaneously, a decrease in hemicellulose content was observed. Chang and Holtzapple [27] postulated that alkali treatment releases hemicellulose as oligomers sensitive among the lignocellulosic compounds, with the reaction of the side groups of hemicellulose occurring first, followed by the hemicellulose backbone [28,29,30]. For P&P sludge, temperatures above 150 °C are suggested, which particularly improve the hydrolysis of hemicellulose [31,32]. The same behavior was shown by Bayr *et al.* [1] after thermal pretreatment, and by Veluchamy *et al.* [26] after electrohydrolysis pretreatment, with an increase in cellulose and a decrease in the hemicellulose content. Also, Lin *et al.* [33] found a degradation rate of hemicellulose of around 50% after pretreatment using P&P sludge, similar to our results.

According to Houfani *et al.* [34], pretreatment helps to eliminate the lignin, the most recalcitrant component of the lignocellulosic biomass, making that biomass more suitable for anaerobic digestion. In fact, lignin content decreased after all pretreatments to between 7 and 11%. Hendriks and Zeeman [31] reported lignin solubilization around 160 °C; however, high temperatures can lead to the formation of a significant amount of inhibitive phenolic compounds. Lower temperatures have the drawback of requiring longer retention time, although this can prevent the formation of the phenolic compounds from lignin. However, temperatures up to 190 °C [1,35] have already been tested for thermal and thermal-alkaline

P&P WAS pretreatment, without inhibition in the anaerobic process due to lignin decomposition.

Theoretical $CH_4$ yield, calculated using the Buswell equation, was improved in all pretreatments tested. Pretreatment increased the potential methane production by at least 100 mL $CH_4$/gVS, when compared to the raw sample. The best theoretical methane production was achieved with thermal-alkaline pretreatment, with results between 376-378 mL $CH_4$/gVS.

Statistically, the major impact of pretreatment was noticed for tCOD, sCOD, TKN, P, VS, hemicellulose and lignin, with emphasis on sample TheAlk-02 (175 °C for 15 min at pH 12). Despite the increase after pretreatment, there are no statistical differences for cellulose content.

**3.2 Effects of Pretreated Sludge on the Anaerobic Digestion Process**

For all BMP tests, the initial pH was adjusted close to 9.0 in order to maintain the same conditions at the beginning of the digestion processes (Table 10). A slight pH drop was expected, due to the production of volatile fatty acids by the acidogenic microorganisms, which are not consumed by the methanogenic microorganisms at the same rate, resulting in an accumulation of acid [36]; if a large decrease in pH occurs, critical levels can be reached which are harmful to the methanogenic process. The presence of nitrogen, especially ammonia (ammonium bicarbonate), helps to prevent the acidification due to its buffering capacity [37,38]. In this study, the final pH remained close to neutral, indicating that there was no excessive process of acid accumulation, which reinforces the suitability of the substrate to the anaerobic digestion process. Similarly, other studies have shown a small drop in the initial pH value, with a final pH of 7.5-8.0 [39,40]. Steinmetz *et al*. [39] also emphasized that a constant pH in the reactor indicated stability of the inoculum, which is crucial for the consistency of the BMP assays.

A high removal of tCOD was observed, from 44.80% (raw) to 57.87-61.87% with samples receiving thermal pretreatment and 73.76-75.72% with samples receiving thermo-alkaline pretreatment. Paranhos *et al*. [40] achieved a tCOD removal of 30.67% to 93.25% when testing different lignocellulosic biomasses, showing that the COD removal efficiency depends on the type of biomass, as well as the food-to-inoculum (F/I) ratio. Dinh and Le [41] showed a COD removal efficiency of 51% after 35 days of digestion using sewage sludge with an initial value of 13,256-16,435 mgCOD/L, demonstrating the capacity of anaerobic digestion to reduce high amounts of organic matter.

**Table 10**. Characteristics of raw and pretreated waste activated sludge from kraft pulp mill after BMP tests

| Parameters | Sample | | | | |
|---|---|---|---|---|---|
| | **Raw** | **The-01** | **The-02** | **TheAlk-01** | **TheAlk-02** |
| Initial pH | 9.05 *a* | 9.03 *a* | 9.01 *a* | 9.07 *a* | 9.04 *a* |
| Final pH | 6.62 *c* | 7.24 *b* | 7.27 *b* | 7.43 *ab* | 7.55 *a* |
| tCOD removal (%) | 44.80 *e* | 57.87 *d* | 61.87 *c* | 75.72 *a* | 73.76 *b* |
| Cellulose (% TS) | 12.98 *a* | 8.53 *b* | 7.03 *c* | 6.62 *d* | 6.52 *d* |
| Hemicellulose (% TS) | 3.84 *a* | 1.82 *b* | 1.71 *bc* | 1.45 *cd* | 1.34 *d* |
| Lignin (% TS) | 17.64 *a* | 11.87 *bc* | 11.28 *c* | 12.14 *b* | 11.51 *bc* |

tCOD: total chemical oxygen demand; TS: total solids
Means that do not share a letter in the same line are significantly different considering 95% confidence

The cellulose and hemicellulose content in the digestate were reduced when comparing the pretreated sludge to the raw sludge. As described by Hendriks and Zeeman [31], temperatures above 150 °C promote the solubilization of the lignocellulosic compounds. For cellulose, reactions with $Na^+$ can cause decrystallization, decreasing the resistance and making it more suitable for hydrolysis [31,42]. In our study, the cellulose content varied from 30.57% TS (raw sludge prior to AD) to 12.98% TS (raw sludge after AD) and 6.52-8.53% TS (pretreated sludge after AD), which means a reduction of 58-79%. Similar results were reported by Lin *et al*. [33], with a degradation efficiency for cellulose of 75-85% after the AD stage using biologically pretreated P&P sludge, and by Paranhos *et al*. [40], using a different lignocellulosic biomass, with a cellulose degradation efficiency of 93%.

For hemicellulose, it has been described that during thermal processes a part of it is hydrolyzed and forms acids, and then these acids are assumed to catalyze the further hydrolysis of the hemicellulose [43]. In our study, the hemicellulose content varied from 5.87% TS (raw sludge prior to AD) to 3.84% TS (raw sludge after AD) and 1.34-1.82% TS (pretreated sludge after AD), representing a reduction of 35-77%. This result is partially superior to that found by Paranhos *et al*. [40], testing a different lignocellulosic biomass, with a maximum hemicellulose removal of 51.80%, and to the results shown by Lin *et al*. [33], who showed a hemicellulose removal of 72% for P&P mill sludge.

Lignin content showed a reduction from 21.98% TS (raw sludge prior to AD) to 17.64% TS (raw sludge after AD) and 11.28-12.14% TS (pretreated sludge after AD), which represents a lignin removal of 20% for raw sludge and 45-49% for pretreated sludge after the AD stage. These lignin removal results are higher than those reported by Lin *et al*. [33], who found a removal of 36% using a microbial consortium to pretreat the P&P mill sludge. This suggests the importance of temperature in the solubilization of lignin, as mentioned by Hendriks and Zeeman [31].

### 3.3 Methane Production

BMP assays were performed in order to measure the real methane production with both raw and pretreated P&P mill WAS. The partial and cumulative methane production rates are presented in Table 11 and Figure 8, respectively. These results show that methane production started slowly and increased from day 5. This first period is characterized by the biomass adaptation, and the initial breakdown of insoluble substrates is performed by the hydrolytic bacteria. Similarly, Spence *et al.* [44] measured the initial period (called the "*lag phase*") between 0 (waste yeast) and 6.8 days (triticale) when analyzing 29 different organic materials. The major methane production occurred during days 11-20, approximately 60% of the total production for all the samples analyzed. Raw sludge started its methane production more slowly, and also achieved the production decay more quickly, demonstrating the major difficulty of the biomass for degrading the substrate under these conditions.

**Table 11**. Partial methane production for days 1-5, 6-10, 11-15, 16-20, 21-25 and 26-30 in BMP tests with raw and pretreated waste activated sludge from kraft pulp mill

| Sample | Methane yield (mL $CH_4$/gVS) | | | | | |
|---|---|---|---|---|---|---|
| | days 1-5 | days 6-10 | days 11-15 | days 16-20 | days 21-25 | days 26-30 |
| Raw | 4 | 19 | 21 | 28 | 14 | 4 |
| The-01 | 11 | 23 | 45 | 62 | 33 | 7 |
| The-02 | 13 | 25 | 47 | 60 | 36 | 13 |
| TheAlk-01 | 14 | 26 | 51 | 70 | 36 | 7 |
| TheAlk-02 | 14 | 24 | 49 | 72 | 35 | 9 |

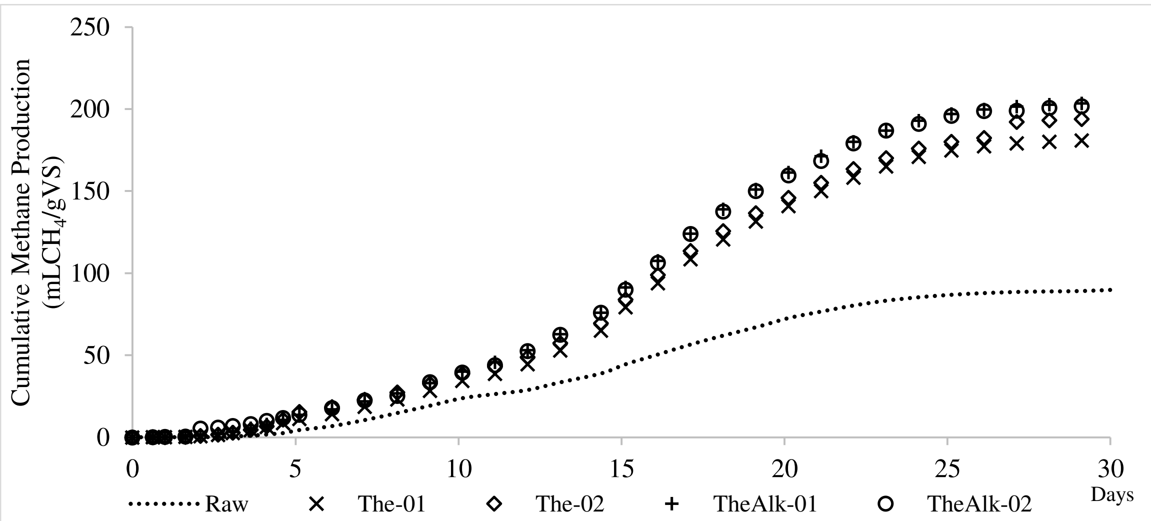


**Figure 8**. Cumulative methane production from BMP assays of kraft pulp mill waste activated sludge.

After 30 days of testing, the cumulative methane production was 90 mL $CH_4$/gVS (Raw), 181 mL $CH_4$/gVS (The-01), 194 mL $CH_4$/gVS (The-02), 204 mL $CH_4$/gVS (TheAlk-

01) and 203 mL $CH_4$/gVS (TheAlk-02). In comparison with the theoretical methane production (Table 9), the influence of pretreatment on the improvement of the methane production rate is clear. For raw sludge, the methane production reached 43% of its theoretical potential, but for the pretreated sludge the methane production increased to 50-54% above its maximum potential. The higher methane production achieved with the pretreated samples can be explained by the higher levels of soluble organic matter, which the microorganisms were able to use immediately. Hydrolysis is probably the limiting step of the AD process, as suggested by other authors [45,46]; by increasing COD solubility, thermal and thermal-alkaline pretreatments enhanced the hydrolysis, providing a greater amount of substrate for downstream microbial metabolism.

Approximately 80% of the total methane production was achieved within the first 20 days of testing, that is, 73 mL $CH_4$/gVS (Raw), 141 mL $CH_4$/gVS (The-01), 146 mL $CH_4$/gVS (The-02), 161 mL $CH_4$/gVS (TheAlk-01) and 160 mL $CH_4$/gVS (TheAlk-02). From this information, two conclusions may be drawn: i) methane production from the raw sludge corresponded to just 50% of that achieved using pretreated WAS; ii) in a 20-day test, the pretreated samples produced more methane than the raw sludge did during 30 days of testing. These results are better than those shown by Lin *et al.* [33], who achieved 76% of the total methane within the first 25 days, using P&P mill sludge pretreated by a microbial consortium. According to those authors, pretreatment could significantly shorten the digestion period by increasing the daily methane production rate, which is important for high productivity in full-scale anaerobic digestion plants.

Using untreated WAS from the same pulp mill, Lopes *et al.* [6] achieved only 47 mL $CH_4$/gVS in BMP assays after 30 days, where the methane production reached just 11.2% of the theoretical potential. This difference may have been caused by the operating conditions: the F/I ratio of 1 $gVS_{substrate}/gVS_{inoculum}$ in our research versus 2 $gVS_{substrate}/gVS_{inoculum}$ adopted by Lopes *et al.* [6], and a BMP incubation temperature of 35 °C in our research versus 55 °C used by Lopes *et al.* [6]. This demonstrates the importance of the operating parameters, which also greatly influence the results.

Despite the significant improvement provided by the sludge pretreatment, the results also revealed that the biodegradability of WAS from P&P mills is inferior to that of sewage sludge. Donoso-Bravo *et al.* [47] achieved a methane production of more than 300 mL $CH_4$/gVS after 20 days of lab tests using sewage sludge pretreated with a hydrolysis reactor connected to a flash tank. The authors explained that the stable woody substrates of P&P WAS, including cellulose and lignin, may be responsible for the low biodegradability when compared with sewage sludge. Nevertheless, the results are superior to those reported for other organic materials, such as: peanut shells (84-157 mL $CH_4$/gVS), coffee husks (116-155 mL $CH_4$/gVS) [40], fresh 4190 grass and silage (125-186 mL $CH_4$/gVS) [48] and grape marc (19-64 mL $CH_4$/gVS) [49]. Table 12 shows the comparison with other studies, where it is demonstrated that pulp mill WAS is a promising substrate for methane production.

**Table 12**. Biochemical methane potential (BMP) for different organic materials

| Pretreatment conditions | Substrate | Theoretical BMP (mL $CH_4$/gVS) | Experimental BMP (mL $CH_4$/gVS) | Ref. |
|---|---|---|---|---|
| Raw | Pulp mill WAS | 211 | 90 | This study |
| Thermal conditions | Pulp mill WAS | 359-360 | 181-194 | This study |
| Thermal-alkaline conditions | Pulp mill WAS | 376-378 | 203-204 | This study |
| Raw | Pulp mill WAS | 519 | 47 | [6] |
| Raw | Pulp/paper mill WAS | - | 66 | [46] |
| Thermal: 80-134 °C, 20-120 min | Pulp/paper mill WAS | - | 60-124 | [46] |
| Raw | Pulp/paper mill WAS | - | 180 | [1] |
| Thermal: 70-150 °C, 10-40 min | Pulp/paper mill WAS | - | 112-134 | [1] |
| Raw | Rice straw | - | 123-270 | [40] |
| Raw | Corn cob | - | 132-291 | [40] |
| Raw | Peanut shell | - | 84-157 | [40] |
| Raw | Coffee husk | - | 116-155 | [40] |
| Raw | Fresh 4190 grass | - | 129-186 | [48] |
| Raw | Silage 4190 grass | - | 125-181 | [48] |
| Raw | Organic waste (fresh) | - | 75 | [50] |
| Raw | Organic waste (1 year) | - | 105 | [50] |
| Raw | Grape marc | - | 19-64 | [49] |
| Raw | Textile sludge | - | 117-244 | [51] |
| Raw | Cattle manure | 537 | 202 | [52] |
| Raw | Milled apple waste | 514 | 297 | [52] |
| Raw | Corn leachate | - | 106 | [53] |
| Raw | Switchgrass | - | 122 | [53] |
| Raw | Manure:switchgrass | - | 208 | [53] |
| Raw | Meat pasta | - | 216 | [53] |
| Raw | Manure:potatoes 75:25 | - | 228 | [53] |
| Raw | Vinegar residue | 473 | 183-243 | [54] |
| Raw | Sewage WAS | - | 206 | [47] |
| Steam explosion: 170 °C, 8 bars, 0-30 min | Sewage WAS | - | 304-324 | [47] |

From an economic standpoint, and considering that kraft mills usually have sources of heat energy (high-pressure steam generated in the recovery boiler) and alkalinity (NaOH used in the wood digesters), the anaerobic process represents a new way to manage WAS with the following advantages: i) a reduction of disposal costs and an environmentally -friendly destination for the sludge (waste); ii) the production of clean and renewable energy; iii) an increase in the amount of electrical energy that can be sold or used in the mill; iv) the provision of power for pumps, sludge dewatering, turbo aerators and other equipment, making the effluent treatment plant self-sufficient in terms of energy.

Moreover, our results suggest that thermal-alkaline pretreatment at pH 11 is sufficient for a satisfactory solubilization for methane production. If the economy in adopting pH 11 instead of pH 12 is negligible on a laboratory scale, in large-scale operations the savings can be significant. Considering the total WAS generated by the mill, estimated at 3360 $m^3$/d, the total amount of NaOH necessary to achieve pH 11 is 4620 kg NaOH/d, versus 5208 kg NaOH/d to achieve pH 12, a difference of almost 600 kg NaOH/d. Since, until now, the studies only focused on pH 12 for alkaline and thermal-alkaline pretreatments [e.g., 1,14], our results show an important improvement for making pretreatment followed by anaerobic digestion suitable and economically advantageous for P&P mills.

## 4 CONCLUSION

Thermal and thermal-alkaline methods for pretreating kraft pulp mill sludge showed an effective solubilization of WAS, required in order to accelerate the hydrolysis phase in the anaerobic digestion process, and also to successfully increase the methane yield and methane production rate. A considerable increase in COD, TKN, $NH_3$-N and VS was demonstrated.

Pretreatment increased both the production rate and yield of methane. After 30-days of testing, the results showed an increase from 90 mL $CH_4$/gVS (raw sludge) to 181-204 mL $CH_4$/gVS (pretreated sludge). Approximately 80% of the total methane was produced in the first 20 days of testing, showing a great improvement for full-scale implementation due to the reduction of the required hydraulic retention time. Thermal-alkaline conditions showed the highest WAS solubilization, and also the best methane yield at operating conditions of 175 °C for 15 min at pH 11.

Along with this pretreatment, the operating conditions of anaerobic digestion (F/I ratio, temperature, etc.) also seem to influence methane production. Therefore, the use and optimization of a pretreatment phase is recommended, as well as the optimization of the anaerobic digestion operating conditions in order to allow its use in the P&P industry.

**REFERENCES**

[1] S. Bayr, P. Kaparaju, J. Rintala, Screening pretreatment methods to enhance thermophilic anaerobic digestion of pulp and paper mill wastewater treatment secondary sludge, Chem Eng J. 223 (1) (2013) 479-486. https://doi.org/10.1016/j.cej.2013.02.119

[2] T. Mahmood, A. Elliot, A review of secondary sludge reduction technologies for the pulp and paper industry, Water Res. 40 (11) (2006) 2093-2112. https://doi.org/10.1016/j.watres.2006.04.001

[3] W. Yuan, H. Yu, Y. Beibei, Comparison of collaborative effects of greenhouse gas emission reduction among main municipal solid waste (MSW) disposal ways - a case study of Tianjin, J. Tianjin Univ. Sci Technol. 4 (2014) 013.

[4] N.D. Park, S.S Helle, R.W. Thring, Combined alkaline and ultrasound pre-treatment of thickened pulp mill waste activated sludge for improved anaerobic digestion, Biomass Bioenerg. 46 (2012) 750-756. https://doi.org/10.1016/j.biombioe.2012.05.014

[5] A. Karlsson, X.B. Truong, J. Gustavsson, B.H. Svensson, F. Nilsson, J. Ejlertsson, Anaerobic treatment of activated sludge from Swedish pulp and paper mills – biogas production potential and limitations, Environ Technol. 32 (14) (2011) 1559-1571. https://doi.org/10.1080/09593330.2010.543932

[6] A.C.P. Lopes, C.M. Silva, A.P. Rosa, F.A. Rodrigues, Biogas production from thermophilic anaerobic digestion of kraft pulp mill sludge, Renewable Energ., 124 (2018) 40.49. https://doi.org/10.1016/j.renene.2017.08.044

[7] T. Meyer, E.A. Edwards, Anaerobic digestion of pulp and paper mill wastewater and sludge, Water Res. 65 (15) (2014) 321-349. https://doi.org/10.1016/j.watres.2014.07.022

[8] A. Tiehm, K. Nickel, M. Zeuhorn, V. Neis, Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization, Water Res. 35 (8) (2001) 2003-2009. http://doi.org/10.1016/S0043-1354(00)00468-1

[9] A. Elliott, T. Mahmood, Pretreatment technologies for advancing anaerobic digestion of pulp and paper biotreatment residues, Water Res. 41 (19) (2007) 4273-4286. https://doi.org/10.1016/j.watres.2007.06.017

[10] M. Kamali, T. Gameiro, M.E.V. Costa, I. Capela, Anaerobic digestion of pulp and paper mill wastes – An overview of the developments and improvement opportunities, Chem. Eng. J. 298 (2016) 162-182. http://dx.doi.org/10.1016/j.cej.2016.03.119

[11] Y. Li, Y. Chen, J. Wu, Enhancement of methane production in anaerobic digestion process: A review, Appl Energ. 240 (2019) 120-137. https://doi.org/10.1016/j.apenergy.2019.01.243

[12] C. Eskicioglu, K.J. Kennedy, R.L. Droste, Enhanced disinfection and methane production from sewage sludge by microwave irradiation, Desalination 248 (1-3) (2009) 279-285. https://doi.org/10.1016/j.desal.2008.05.066

[13] A. Elliott, T. Mahmood, Comparison of Mechanical Pretreatment Methods for the Enhancement of Anaerobic Digestion of Pulp and Paper Waste Activated Sludge, Water Environ Res. 84 (6) (2012) 497-505. https://doi.org/10.2175/106143012X13347678384602

[14] N. Wood, H. Tran, E. Master, Pretreatment of pulp mill secondary sludge for high-rate anaerobic conversion to biogas, Bioresource Technol. 100 (23) (2009) 5729-5735. https://doi.org/10.1016/j.biortech.2009.06.062

[15] APHA/AWWA/WPC, Standard methods for the examination of water and wastewater, 22. ed. Washington: American Public Health Association, American Water Works Association, Water Environment Federation; 1360 pp. 2012. ISBN 978-087553-013-0

[16] EPA, 821-R-01-004 January 2001 - Method 1687, Total Kjeldahl Nitrogen in Water and Biosolids by Automated Colorimetry with Preliminary Distillation/Digestion. DRAFT January 2001.

[17] EPA, 821-R-01-012 January 2001 - Method 1689. Ammonia-N in Water and Biosolids by Ion-Selective Electrode Potentiometry with Preliminary Distillation DRAFT January 2001.

[18] TAPPI, Technical Association of the Pulp and Paper Industry – TAPPI. T 249 cm-85 (R2009), Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography. Atlanta: TAPPI Standard Method; 2009.

[19] TAPPI, Technical Association of the Pulp and Paper Industry – TAPPI. Standard T 222 om-11: Acid insoluble lignin in wood and pulp. Atlanta: TAPPI Standard Method; 2011.

[20] B.E. Rittmann, P.L. McCarty, Environmental Biotechnology: Principles and Applications, Tata McGraw Hill Education Private Limited; 768 pp. 2012. ISBN 1260440591

[21] I. Angelidaki, M. Alves, D. Bolzonella, L. Borzacconi, J.L. Campos, A.J. Guwy, S. Kalyuzhnyi, P. Jenicek, J.B. van Lier, Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays, Water Sci Technol. 59 (5) (2009) 927-934. https://doi.org/10.2166/wst.2009.040

[22] C. Holliger, M. Alves, D. Andrade, I. Angelidaki, S. Astals, U. Baier, C. Bougrier, P. Buffière, M. Carballa, V. de Wilde, F. Ebertseder, B. Fernández, E. Ficara, I. Fotidis, J.C. Frigon, H.F. de Laclos, D.S.M. Ghasimi, G. Hack, M. Hartel, J. Heerenklage, I.S. Horvath, P. Jenicek, K. Koch, J. Krautwald, J. Lizasoain, J. Liu, L. Mosberger, M. Nistor, H. Oechsner, J.V. Oliveira, M. Paterson, A. Pauss, S. Pommier, I. Porqueddu, F. Raposo, T. Ribeiro, F.R. Pfund, S. Strömberg, M. Torrijos, M. van Eekert, J. van Lier, H. Wedwitschka, I. Wierinck, Towards a standardization of biomethane potential tests, Water Sci Technol. 74 (11) (2016) 2515-2522. https://doi.org/10.2166/wst.2016.336

[23] A.C.P. Lopes, Biogas production potential from kraft pulp mill sludge, Thesis, Universidade Federal de Viçosa, Brazil (2017) 99p.

[24] C.A.L. Chernicharo, Reatores anaeróbios, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil, 2nd ed., 1997.

[25] Y. Lin, D. Wang, S. Wu, C. Wang, Alkali pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge, J Hazard Mater. 170 (1) (2009) 366-373. https://doi.org/10.1016/j.jhazmat.2009.04.086

[26] C. Veluchamy, V.W. Raju, A.S. Kalamdhad, Prerequisite – An electrohydrolysis pretreatment for anaerobic digestion of lignocellulose waste material, Bioresource Technol. 253 (2017) 274-280. https://doi.org/10.1016/j.biortech.2017.03.137

[27] V.S Chang, M.T. Holtzapple, Fundamental factors affecting biomass enzymatic reactivity, Appl Biochem Biotechnol. 84 (2000) 5-37. https://doi.org/10.1385/ABAB:84-86:1-9:5

[28] S.L. Levan, R.J. Ross, J.E. Winandy, Effects of fire retardant chemicals on bending properties of wood at elevated temperatures. Research Paper FPL-RP498. Madison, WI: U.S. Department of agriculture, Forest service, Forest Products Laboratory, 1990.

[29] J.E. Winandy, Effects of fire retardant treatments after 19 months of exposure at 150F (66C). Res. Note FPL-RN-0264. U.S. Department of agriculture, Forest Service, Forest Products Laboratory, Madison, WI., 1995.

[30] M.S. Sweet, J.E. Winandy, Influence of degree of polymerization of cellulose and hemicellulose on strength loss in fire-retardant-treated southern pine, Holzforschung 53 (3) (1999) 311-317. https://doi.org/10.1515/HF.1999.051

[31] A.T.W.M. Hendriks, G. Zeeman, Pretreatments to enhance the digestibility of lignocellulosic biomass, Bioresource Technol. 100 (1) (2009) 10-18. https://doi.org/10.1016/j.biortech.2008.05.027

[32] V. Fernandez-Cegri, M.A. de la Rubia, F. Raposo, R. Borja, Effect of hydrothermal pretreatment of sunflower oil cake on biomethane potential focusing on fibre composition, Bioresource Technol. 123 (2012) 424-429. https://doi.org/10.1016/j.biortech.2012.07.111

[33] Y. Lin, J. Liang, C. Zeng, D. Wang, H. Lin, Anaerobic digestion of pulp and paper mill sludge pretreated by microbial consortium OEM1 with simultaneous degradation of lignocellulose and chlorophenols, Renewable Energ, 108 (2017) 108-115. https://doi.org/10.1016/j.renene.2017.02.049

[34] A.A. Houfani, N. Anders, A.C. Spiess, P. Baldrian, S. Benallaoua, Insights from enzymatic degradation of cellulose and hemicellulose to fermentable sugars – a review, Biomass Bioenerg. 134 (2020). https://doi.org/10.1016/j.biombioe.2020.105481

[35] X.M. Huang, Enhancing Anaerobic Digestion of Pulp and Paper Mill Biosludge using Thermal Treatment in a Bench-scale System, Thesis, University of Toronto, Canada (2015), 115p.

[36] Y. Zhou, Z. Zhang, T. Nakamoto, Y. Li, Y. Yang, M. Utsumi, N. Sugiura, Influence of substrate-to-inoculum ratio on the batch anaerobic digestion of bean curd refuse-okara under mesophilic conditions, Biomass Bioenerg. 35 (7) (2011) 3251-3256. https://doi.org/10.1016/j.biombioe.2011.04.002

[37] O. Lahav, B.E. Morgan, Titration methodologies for monitoring of anaerobic digestion in developing countries - a review, J. Chem. Technol. Biot. 79 (2004) 1331-1341. https://doi.org/10.1002/jctb.1143

[38] M. Murto, L. Bjornsson, B. Mattiasson, Impact of food industrial waste on anaerobic co-digestion of sewage sludge and pig manure, J. Environ. Manage. 70 (2) (2004) 101-107. https://doi.org/10.1016/j.jenvman.2003.11.001

[39] R.L.R. Steinmetz, M.P. Mezzari, M.L.B. Silva, A. Kunz, A.C. Amaral, D.C. Tápparo, H.M. Soares, Enrichment and acclimation of an anaerobic mesophilic microorganism's inoculum for standardization of BMP assays, Bioresource Technol. 219 (2016) 21-28. https://doi.org/10.1016/j.biortech.2016.07.031

[40] A.G.O. Paranhos, O.F.H. Adarme, G.F. Barreto, S.Q. Silva, S.F. Aquino, Methane production by co-digestion of poultry manure and lignocellulosic biomass: Kinetic and energy assessment, Bioresource Technol. 300 (2020). https://doi.org/10.1016/j.biortech.2019.122588

[41] N.T. Dinh, N.H. Le, The Performance of an Anaerobic Digester Treating BioSludge Generated from a Municipal Wastewater Treatment Plant in a Pilot Scale, Chem Eng Transactions, 78 (2020). https://doi.org/10.3303/CET2078091

[42] C. Jiao, J. Xiong, Accessibility and morphology of cellulose fibres trated with sodium hydroxide, BioRes. 9 (4) (2014) 6504-6513.

[43] D. Gregg, J.N. Saddler, The Influence of the Substrate (Softwood/Hardwood) on the Pretreatment, Fractionation and Hydrolysis Steps of a Bioconversion Process, Abstr. Pap. Am. Chem. Soc. 209 Meet, Pt.2, BTEC120 (1995).

[44] A. Spence, E.B. Madrigal, R. Deshpande, Y.B. Fernández, Evaluation of anaerobic digestibility of energy crops and agricultural by-products, Biores Technol Reports. 5 (2019) 243-250. https://doi.org/10.1016/j.biteb.2018.11.004

[45] M. Saha, C. Eskicioglu, J. Marin, Microwave, ultrasonic and chemo-mechanical pretreatments for enhancing methane potential of pulp mill wastewater treatment sludge, Bioresource Technol. 102 (17) (2011) 7815-7826. https://doi.org/10.1016/j.biortech.2011.06.053

[46] V. Kinnunen, A. Yla-Outinen, J. Rintala, Mesophilic anaerobic digestion of pulp and paper industry biosludge-long-term reactor performance and effects of thermal pretreatment, Water Res. 87 (15) (2015) 105-111. https://doi.org/10.1016/j.watres.2015.08.053

[47] A. Donoso-Bravo, S. Pérez-Elvira, E. Aymerich, F. Fdz-Polanco, Assessment of the influence of thermal pre-treatment time on the macromolecular composition and anaerobic biodegradability of sewage sludge, Bioresource Technol. 102 (2) (2011) 660-666. https://doi.org/10.1016/j.biortech.2010.08.035

[48] A. Sonwai, P. Pholchan, A. Nuntaphan, P. Juangjandee, N. Totarat, Biochemical Methane Potential of Fresh and Silage 4190 Grass Under Thermophilic Conditions, Thai Environ Eng. J. 33(1) (2019) 21-29.

[49] K.C.D. Silva, M.C.C. Amorim, R.S. Galvão, Y.B.O. Gonçalves, P.T.S. Silva, E.S.C. Barros, Effect of the inoculum/substrate ratio on the biochemical methane potential (BMP) of grape marc, Rev Amb Agua. 15 (5) (2020). https://doi.org/10.4136/ambi-agua.2541

[50] W.N. Schirmer, J.F.T. Jucá, A.R.P. Schuler, S. Holanda, L.L. Jesus, Methane production in anaerobic digestion of organic waste from Recife (Brazil) landfill: evaluation in refuse of diferent ages, Brazilian J Chem Eng. 31 (2) (2014), 373-384. https://doi.org/10.1590/0104-6632.20140312s00002468

[51] P. Kumar, S. Samuchiwal, A. Malik, Anaerobic digestion of textile industries wastes for biogas production, Biomass Conv. Bioref. 10 (2020) 715-724. https://doi.org/10.1007/s13399-020-00601-8

[52] P.P. Nieto, D. Hidalgo, R. Irusta, D. Kraut, Biochemical methane potential (BMP) of agro-food wastes from the Cider Region (Spain), Water Sci Technol. 66 (9) (2012) 1842-1848. https://doi.org/10.2166/wst.2012.372

[53] R.A. Labatut, L.T. Angenent, N.R. Scott, Biochemical methane potential and biodegradability of complex organic substrates, Bioresource Technol. 102 (3) (2011) 2255-2264. https://doi.org/10.1016/j.biortech.2010.10.035

[54] L. Feng, Y. Li, C. Chen, X. Liu, X. Xiao, X. Ma, R. Zhang, Y. He, G. Liu, Biochemical Methane Potential (BMP) of Vinegar Residue and the Influence of Feed to Inoculum Ratios on Biogas Production, BioRes. 8 (2) (2013) 2487-2498.

# CONCLUSÕES GERAIS E RECOMENDAÇÕES FINAIS

A digestão anaeróbia de lodo secundário proveniente de fábricas de P&P, otimizada pela solubilização prévia promovida pelo pré-tratamento, mostra-se como uma opção a ser avaliada para o gerenciamento de tais resíduos.

O elevado número de artigos publicados nesta temática demonstra o interesse da comunidade científica e da indústria no aprimoramento da tecnologia anaeróbia para tratamento dos lodos. Os resultados, apesar de discrepantes, são promissores e encorajam a continuidade do avanço científico por meio do desenvolvimento de novas pesquisas.

Com base nos parâmetros avaliados, os métodos mecânico, térmico e térmico-alcalino promoveram a solubilização da matéria orgânica, notadamente da $DBO_5$, DQOs e nutrientes (nitrogênio e fósforo). Como reflexo, o potencial teórico de produção de metano também apresentou elevação, dando o primeiro indicativo do efeito positivo do pré-tratamento quando se almeja o incremento na produção de metano.

Em testes em bancada que simulam a digestão anaeróbia, foi possível demonstrar o aumento real na produção de metano ocasionado pela aplicação do pré-tratamento. Além do aumento da geração total de metano, foi possível demonstrar o adiantamento da curva de produção, ou seja, os efeitos da solubilização prévia do lodo também se dão na aceleração do processo de geração de biogás.

Os efeitos do pré-tratamento incidem sobre a etapa inicial da digestão anaeróbia, caracterizada pela hidrólise da matéria orgânica complexa por meio da ação de enzimas extracelulares excretadas por bactérias estritamente anaeróbias, suprindo os substratos necessários às bactérias acidogênicas. Quando a matéria orgânica presente é complexa e de difícil degradação, a hidrólise tem grande importância na velocidade global de degradação, podendo ser considerada como etapa limitante da velocidade da digestão anaeróbia. Os ganhos na produção total de metano e na aceleração do processo são explicados justamente pelo fato de que o pré-tratamento causa a quebra dos complexos orgânicos, conforme demonstrado nos testes de solubilização.

Para um entendimento mais profundo do processo, recomenda-se a execução de testes em escala piloto, visando estudar variáveis importantes ao processo, como a carga orgânica volumétrica inicial, a alcalinidade e a geração de ácidos orgânicos. Além disso, levanta-se a importância do aprofundamento dos efeitos do pré-tratamento no desenvolvimento da microbiota anaeróbia, sendo de interesse a realização de testes em escala molecular para caracterização e quantificação dos grupos de interesse.

**REFERÊNCIAS GERAIS**

Brasil. Lei n. 13.576, de 26 de dezembro de 2017. Dispõe sobre a Política Nacional de Biocombustíveis (RenovaBio) e dá outras providências. Diário oficial da união, 27/12/2017.

Gomes, G.V.; Suda, S.J.; Rosa, A.P.; Rodrigues, F.A. Estudo da produção de energia elétrica a partir de biogás com e sem purificação de estação de tratamento de esgotos. *The Journal of Engineering and Exact Sciences*, v. 3, n. 7, 2017.

Ibá. Indústria Brasileira de Árvores. Cenários Ibá 45, feb. 2018. http://iba.org/images/shared/Cenarios/45_Cenarios.pdf

Kamali, M.; Gameiro, T.; Costa, M.E.V.; Capela, I. Anaerobic digestion of pulp and paper mill wastes – An overview of the developments and improvement opportunities. *Chemical Engineering Journal*, v. 298, n. 15, p. 162-182, 2016.

Meyer, T.; Edwards, E. A. Anaerobic digestion of pulp and paper mill wastewater and sludge. *Water Research*, v. 65, p. 321–349, 2014.

# APPENDIX A

**Table S1**. Results of estimating single-stage and high-rate anaerobic digester volume and performance considering pretreated and raw waste activated sludge from a kraft pulp mill

| **SRT (d)** | **Q ($m^3/d$)** | **$V_d$ ($m^3$)** | **Pretreated sludge** | | | | **Raw sludge** | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | **$S_0$ (kg/d)** | **S (kg/d)** | **$P_x$ (kg/d)** | **V $CH_4$ ($m^3/d$)** | **$S_0$ (kg/d)** | **S (kg/d)** | **$P_x$ (kg/d)** | **V $CH_4$ ($m^3/d$)** |
| considering 100% of the surplus activated sludge treated via anaerobic digestion | | | | | | | | | | |
| 8 | | 26880 | | | 609 | **2912** | | | 130 | **621** |
| 10 | | 33600 | | | 581 | **2952** | | | 124 | **629** |
| 12 | | 40320 | | | 555 | **2989** | | | 118 | **637** |
| 14 | 3360 | 47040 | 13490 | 4047 | 532 | **3022** | 2876 | 863 | 113 | **644** |
| 16 | | 53760 | | | 510 | **3052** | | | 109 | **651** |
| 18 | | 60480 | | | 491 | **3081** | | | 105 | **657** |
| 20 | | 67200 | | | 472 | **3107** | | | 101 | **662** |
| considering 75% of the surplus activated sludge treated via anaerobic digestion | | | | | | | | | | |
| 8 | | 20160 | | | 457 | **2184** | | | 97 | **466** |
| 10 | | 25200 | | | 436 | **2214** | | | 93 | **472** |
| 12 | | 30240 | | | 417 | **2241** | | | 89 | **478** |
| 14 | 2520 | 35280 | 10118 | 3035 | 399 | **2266** | 2157 | 647 | 85 | **483** |
| 16 | | 40320 | | | 383 | **2289** | | | 82 | **488** |
| 18 | | 45360 | | | 368 | **2311** | | | 78 | **493** |
| 20 | | 50400 | | | 354 | **2330** | | | 75 | **497** |
| considering 50% of the surplus activated sludge treated via anaerobic digestion | | | | | | | | | | |
| 8 | | 13440 | | | 305 | **1456** | | | 65 | **310** |
| 10 | | 16800 | | | 291 | **1476** | | | 62 | **315** |
| 12 | | 20160 | | | 278 | **1494** | | | 59 | **319** |
| 14 | 1680 | 23520 | 6745 | 2024 | 266 | **1511** | 1438 | 431 | 57 | **322** |
| 16 | | 26880 | | | 255 | **1526** | | | 54 | **325** |
| 18 | | 30240 | | | 245 | **1540** | | | 52 | **328** |
| 20 | | 33600 | | | 236 | **1553** | | | 50 | **331** |

SRT: solids retention time; Q: sludge flowrate; $V_d$: anaerobic digester volume; $S_0$: BOD ultimate in influent; S: BOD ultimate in effluent; $P_x$: net mass of cell tissue produced per day; V $CH_4$: volume of methane produced at 35 °C

# APPENDIX B

**Table S1.** Results for Ryan-Joiner Normality Test for Total (tCOD) and Soluble (sCOD) Chemical Oxygen Demand, Biochemical Oxygen Demand ($BOD_5$), Total Phosphorus (P), Total Kjeldahl Nitrogen (TKN) and Ammonia-Nitrogen ($NH_3$-N)

| Source of variation | Mean | StDev | N | RJ | *p*-value |
|---|---|---|---|---|---|
| tCOD | 10,103 | 1,205 | 99 | 0.991 | > 0.100 |
| sCOD | 8,902 | 1,918 | 99 | 0.906 | < 0.010 |
| $BOD_5$ | 2,615 | 412 | 99 | 0.777 | < 0.010 |
| P | 63.56 | 8.058 | 102 | 0.597 | < 0.010 |
| TKN | 297.7 | 48.51 | 102 | 0.565 | < 0.010 |
| $NH_3$-N | 33.56 | 9.005 | 102 | 0.755 | < 0.010 |

**Table S2.** Statistical Results for Total (tCOD) and Soluble (sCOD) Chemical Oxygen Demand and Biochemical Oxygen Demand ($BOD_5$)

| Pretreatment | tCOD (g/L) (1) | sCOD (g/L) (2) | $BOD_5$ (g/L) (2) |
|---|---|---|---|
| Raw sludge | $7.55 \pm 0.17^{2.29}{}_{i}$ | $1.11 \pm 0.02^{1.95}{}_{e}$ | $0.57 \pm 0.03^{6.02}{}_{d}$ |
| M: 990 kJ | $8.43 \pm 0.07^{0.86}{}_{hi}$ | $7.30 \pm 0.11^{1.55}{}_{e}$ | $2.43 \pm 0.10^{4.05}{}_{cd}$ |
| M: 1980 kJ | $8{,}747 \pm 85^{0.97}{}_{h}$ | $7.39 \pm 0.08^{1.06}{}_{e}$ | $2.60 \pm 0.07^{2.80}{}_{bcd}$ |
| M: 3960 kJ | $9.12 \pm 0.32^{3.46}{}_{fgh}$ | $7.50 \pm 0.13^{1.72}{}_{de}$ | $2.57 \pm 0.12^{4.55}{}_{bcd}$ |
| T: 150 °C, 15 min | $8.81 \pm 0.17^{1.92}{}_{gh}$ | $7.331 \pm 0.15^{2.07}{}_{e}$ | $2.56 \pm 0.22^{8.69}{}_{bcd}$ |
| T: 150 °C, 30 min | $9.13 \pm 0.37^{4.04}{}_{fgh}$ | $7.75 \pm 0.16^{2.08}{}_{de}$ | $2.68 \pm 0.08^{3.07}{}_{bc}$ |
| T: 150 °C, 60 min | $10.22 \pm 0.57^{5.59}{}_{cde}$ | $10.40 \pm 0.30^{2.93}{}_{ab}$ | $2.77 \pm 0.18^{6.52}{}_{ab}$ |
| T: 175 °C, 15 min | $10.57 \pm 0.77^{7.27}{}_{bcde}$ | $9.66 \pm 0.20^{2.04}{}_{abc}$ | $2.34 \pm 0.07^{3.01}{}_{cd}$ |
| T: 175 °C, 30 min | $10.82 \pm 0.55^{5.10}{}_{bcd}$ | $10.73 \pm 0.49^{4.58}{}_{a}$ | $2.76 \pm 0.04^{1.28}{}_{ab}$ |
| T: 175 °C, 60 min | $11.04 \pm 0.20^{1.79}{}_{bcd}$ | $9.37 \pm 0.34^{3.58}{}_{bcd}$ | $2.74 \pm 0.06^{2.07}{}_{ab}$ |
| T: 200 °C, 15 min | $9.78 \pm 0.24^{2.50}{}_{efg}$ | $8.92 \pm 0.24^{2.72}{}_{cde}$ | $2.52 \pm 0.01^{3.84}{}_{cd}$ |
| T: 200 °C, 30 min | $10.07 \pm 0.38^{3.73}{}_{def}$ | $9.33 \pm 0.29^{3.14}{}_{bcd}$ | $2.64 \pm 0.06^{2.17}{}_{bc}$ |
| T: 200 °C, 60 min | $10.80 \pm 0.32^{2.98}{}_{bcd}$ | $9.76 \pm 0.33^{3.37}{}_{abc}$ | $2.74 \pm 0.07^{2.73}{}_{ab}$ |
| TA: 150 °C, 15 min, pH 11 | $10.85 \pm 0.37^{3.43}{}_{bcd}$ | $9.21 \pm 0.42^{4.52}{}_{bcd}$ | $2.77 \pm 0.16^{5.78}{}_{ab}$ |
| TA: 150 °C, 15 min, pH 12 | $11.35 \pm 0.82^{7.26}{}_{ab}$ | $9.89 \pm 0.86^{8.69}{}_{abc}$ | $2.90 \pm 0.13^{4.35}{}_{a}$ |
| TA: 175 °C, 15 min, pH 11 | $11.09 \pm 0.77^{6.92}{}_{bc}$ | $10.32 \pm 0.65^{6.27}{}_{ab}$ | $2.94 \pm 0.16^{5.31}{}_{a}$ |
| TA: 175 °C, 15 min, pH 12 | $12.07 \pm 0.62^{5.09}{}_{a}$ | $11.46 \pm 0.74^{6.48}{}_{a}$ | $2.89 \pm 0.09^{3.19}{}_{a}$ |

(1) compared with Tukey test; (2) compared with Dunn test

Mean ± standard deviation $^{\text{coefficient of variation}}$ *statistical test*

Means that do not share a letter are significantly different considering 95% confidence

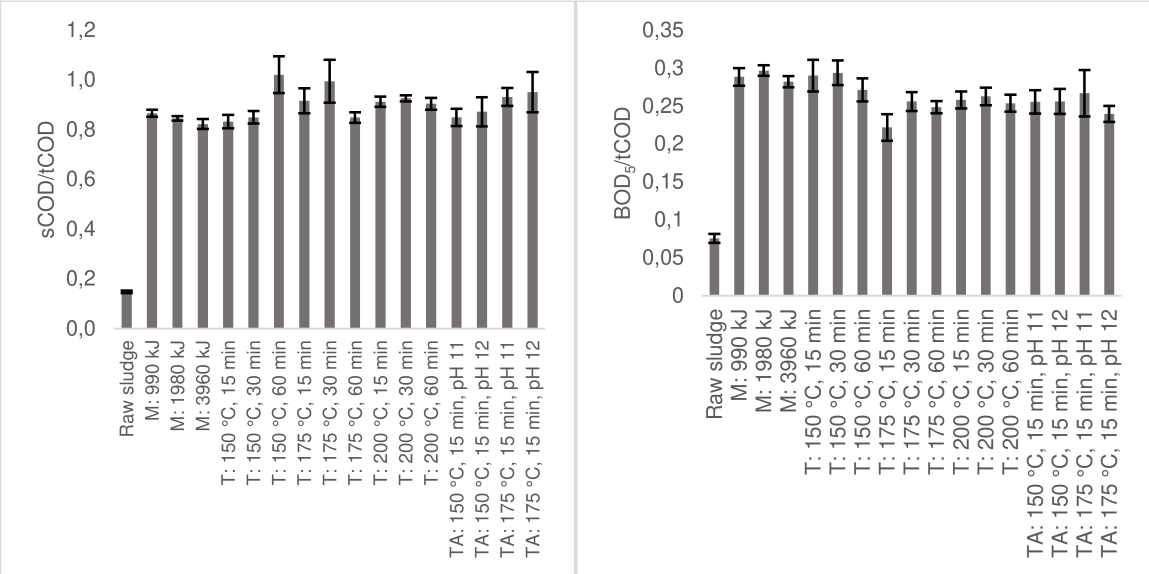


**Figure S1.** Soluble chemical oxygen demand versus total chemical oxygen demand (sCOD/tCOD) and biochemical oxygen demand versus total chemical oxygen demand ($BOD_5$/tCOD) before and after pretreatment tests

**Table S3.** Statistical Results for Total Kjeldahl Nitrogen (TKN), Ammonia-Nitrogen ($NH_3$-N) and Total Phosphorus (P)

| Pretreatment | TKN (1) | $NH_3$-N (1) | P (1) |
|---|---|---|---|
| Raw sludge (soluble) | $29 \pm 2^{5.97}_{f}$ | un(2) | $19 \pm 1^{5.11}_{f}$ |
| Raw sludge (total) | $366 \pm 7^{2.02}_{a}$ | un(2) | $67 \pm 1^{2.23}_{a}$ |
| M: 990 kJ | $297 \pm 4^{1.30}_{ef}$ | $32 \pm 1^{3.80}_{ef}$ | $63 \pm 1^{1.44}_{ef}$ |
| M: 1980 kJ | $300 \pm 1^{0.48}_{def}$ | $32 \pm 1^{4.29}_{ef}$ | $63 \pm 1^{1.90}_{def}$ |
| M: 3960 kJ | $299 \pm 2^{0.64}_{ef}$ | $33 \pm 1^{4.23}_{ef}$ | $64 \pm 1^{1.76}_{cdef}$ |
| T: 150 °C, 15 min | $296 \pm 5^{1.59}_{ef}$ | $33 \pm 2^{7.05}_{ef}$ | $63 \pm 2^{2.56}_{cdef}$ |
| T: 150 °C, 30 min | $297 \pm 5^{1.77}_{ef}$ | $35 \pm 3^{7.85}_{cde}$ | $63 \pm 1^{2.31}_{cdef}$ |
| T: 150 °C, 60 min | $307 \pm 5^{1.72}_{abcd}$ | $35 \pm 2^{6.54}_{bcde}$ | $65 \pm 1^{2.22}_{abcd}$ |
| T: 175 °C, 15 min | $302 \pm 5^{1.58}_{cdef}$ | $34 \pm 2^{7.08}_{cdef}$ | $64 \pm 1^{2.14}_{bcde}$ |
| T: 175 °C, 30 min | $305 \pm 6^{1.82}_{bcde}$ | $33 \pm 3^{9.09}_{def}$ | $65 \pm 1^{2.14}_{abc}$ |
| T: 175 °C, 60 min | $309 \pm 5^{1.70}_{abc}$ | $37 \pm 2^{6.17}_{abc}$ | $66 \pm 2^{2.41}_{ab}$ |
| T: 200 °C, 15 min | $301 \pm 6^{2.04}_{cdef}$ | $34 \pm 2^{6.15}_{cde}$ | $63 \pm 2^{2.37}_{cdef}$ |
| T: 200 °C, 30 min | $308 \pm 5^{1.56}_{abc}$ | $37 \pm 3^{7.05}_{abcd}$ | $65 \pm 2^{2.62}_{bcde}$ |
| T: 200 °C, 60 min | $309 \pm 7^{2.11}_{abc}$ | $37 \pm 2^{5.43}_{abc}$ | $66 \pm 2^{2.26}_{ab}$ |
| TA: 150 °C, 15 min, pH 11 | $307 \pm 4^{1.47}_{abc}$ | $39 \pm 2^{4.61}_{ab}$ | $65 \pm 2^{2.90}_{abcde}$ |
| TA: 150 °C, 15 min, pH 12 | $310 \pm 2^{0.59}_{ab}$ | $39 \pm 1^{3.46}_{a}$ | $66 \pm 2^{2.51}_{ab}$ |
| TA: 175 °C, 15 min, pH 11 | $310 \pm 2^{0.66}_{ab}$ | $39 \pm 2^{4.69}_{ab}$ | $67 \pm 2^{2.31}_{a}$ |
| TA: 175 °C, 15 min, pH 12 | $309 \pm 1^{0.38}_{ab}$ | $39 \pm 1^{3.61}_{ab}$ | $67 \pm 2^{2.48}_{a}$ |

(1) compared with Dunn test; (2) undetected

Mean ± standard deviation $^{\text{coefficient of variation}}$ *statistical test*

Means that do not share a letter are significantly different considering 95% confidence