Biogas Production from Paper Mill Sludge as a Potential Source of Organic Matter

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The waste from the paper industry continues to increase globally, notably the generated paper mill sludge (PMS), which constitutes a challenging residue to treat and typically ends up in landfills. The recovery of this sludge in the energy sector is very interesting as they are composed of lignocellulosic materials that are highly favorable for methane production in anaerobic environments. The sludge is collected at the unit affiliated with the leading paper production company Faderco in Setif. A physico-chemical characterization of the PMS is carried out (pH, total solids content and volatile solids, ammoniacal nitrogen, alkalinity, and organic acid content). Anaerobic digestion tests are also conducted on both wet and dry phases to determine the methanogene potential. The biogas production yield is 520 m3/ton in the dry basis and 200 m3/ton in the wet basis. As for the methane yield, the value is 320 m3/ton in the dry basis and 120 m3/ton in the wet basis. In comparison of PMS with other substrates cereal straw, used grease, agricultural residues, this residue is estimated to be a potential substrate for the methane production.

Keywords: Paper mill sludge, anaerobic digestion, biogas, recovery,

methanogene potential.

1. Introduction

The paper industry is considered as one of the most polluting industrial sectors in the world. It is typically a large consumer of energy and water [1]. The production of paper mill sludge (PMS) is estimated to vary from 0.3 m^3 to 1 m^3 of sludge per tonne of paper produced [2]. This sludge is traditionally disposed through many methods such as landfilling, incineration, or agricultural spreading, which are often regarded as less sustainable and more environmentally harmful management options [3-4].

The PMS has been recovered in several areas such as production of energy (biogas [5]), biofuel [6], in agriculture (fertilizers [7]), manufacturing construction materials [8]), manufacturing of chemicals [9]), wastewater treatment for various pollutants (bioadsorption [10-11])...etc.

The anaerobic digestion is such an interesting process for the treatment of waste and the management of resources simultaneously. To carry out this process, various groups of naturally available bacteria are used to perform biodegradation and produce renewable energy from organic materials [12]. Several lignocellulosic wastes have been recovered for methane production, such as: orange peels [13], cereal straw [14], corn stalks [15], green leaves [15], and garden waste [15]... etc.

Energy production from paper mill sludge represents an interesting industrial opportunity; recent studies have demonstrated the technical feasibility of anaerobic digestion in biogas production [16-20]. After pretreatment, cellulose-rich paper mill sludges are converted into various products, such as glucose, ethanol, hydrogen, lactic acid, acetic acid, methane, waste biosorbents, as well as numerous other chemicals and materials [21-23]. Unlike anaerobic digestion of wastewater, anaerobic digestion of paper mill sludge is still in its early stages [24]. It is in this context that the present work has been conducted with the aim of valorizing the PMS to produce renewable energy (biogas).

2. MATERIALS AND METHODS

2.1. Preparation

The paper mill sludge (PMS) collected from the FADERCO industrial unit (Setif) is dried in a Memmert oven at 105°C for 24 hours. It is subsequently ground and sieved to obtain fine particles smaller than 100µm. The resulting raw powder (RP) is stored in polyethylene (PET) bottles in a desiccator until a further use.

2.2. Characterization

Many analytical methods are used to determine pH, total solids (TS) and volatile solids (VS) content, ammoniacal nitrogen, alkalinity, and organic acid content.

2.2.1. pH

The pH of the raw power plays an important role during the anaerobic digestion process, where it is measured before and after the process. Three samples of 1 g are introduced into 3 separate beakers, and a volume of 10 ml of distilled water is added to each sample. The mixture is homogenized by stirring for 5 minutes. The pH of the solution is measured using an Inolab pH 7110 pH meter [25].

2.2.2. Total solids (TS) and volatile solids (VS) contents

The TS and VS are determined by analytical gravimetry. This analysis is carried out to determine the organic matter content (VS) of RP, which is used to calculate the estimated mass for tests of the anaerobic digestion process, according to the following equations:

$$\mathrm{TS}\left(\frac{\mathrm{g}}{\mathrm{Kg}}\right)=\frac{(\text{Dry sample weight(g) (After drying)}}{(\text{Wet Sample mass (Before drying)}*0.001\text{ (kg)})} \quad (1)$$

$$\mathrm{VS}\left(\frac{\mathrm{g}}{\mathrm{Kg}}\right)=\text{ total solids (g/Kg)}-\text{ash(g/Kg)} \quad (2)$$

2 g of raw powder is dried at 105°C for 24 hours and then incinerated at 550°C in a muffle furnace (SHIMADZU) for 2 hours to determine the content of non-volatile solids (ashes) and volatile solids (organic matter).

2.2.3. Ammoniacal nitrogen

Organic nitrogen is determined using the Kjeldahl technique before and after anaerobic digestion. Mineralization of the raw powder is necessary to convert the organic nitrogen present in the sludge into mineral nitrogen according to the following steps:

-1 g of the raw powder is introduced into a Kjeldahl flask with the addition of 0.5 g of digestive catalyst (copper sulfate and potassium sulfate), and 10 ml of concentrated sulfuric acid.

-The flask is heated to 350°C for 3 hours. After digestion, the flask is cooled to room temperature.

-The contents of the flask are transferred to a distillation apparatus to release ammonia as a gas, an alkaline solution (caustic soda) is added.

The distillate containing ammonia is ready to be titrated with a solution of HCl (0.01 M), a colored indicator (phenolphthalein) is added to the distillate [26].

2.2.4. Alkalinity

Alkalinity is an important parameter during anaerobic digestion [27]. It is related to pH balance and the stability of the anaerobic digestion process to ensure optimal biogas production [27].

The determination of the alkalinity of the raw powder is done by titration. 0.1 g of the raw powder is introduced into a beaker, and 25 ml of water is added. The mixture is homogenized by stirring for 15 minutes, then filtered and titrated with HCl (0.01 N). The alkalinity is calculated and expressed in terms of calcium carbonate equivalent ($CaCO_3$) using the following equation [28]:

C = (A*N*50000)/B (3)

C: Total alkalinity ($CaCO_3$ mg/L).

A: Volume of HCl solution used (ml).

B: Volume of sample used (ml).

50000: Weight of one equivalent of $CaCO_3$ expressed in mg.

2.2.5. Organic acids

The analysis of acids present in the raw powder before and after anaerobic digestion is performed using high-performance liquid chromatography (HPLC), HPLC Machine, LC-4000. Solvent extraction (methanol) is carried out on a mass of 0.5g of the raw powder for 3 hours, and the solvent is evaporated using a rotary evaporator. Standard solutions of various acids are prepared to calibrate the HPLC equipment. The sample and standards are injected into the HPLC system, and the data obtained are analyzed using chromatographic analysis software. The same steps realized on the digestate recovered after anaerobic digestion [29].

2.3. Anaerobic digestion

2.3.1. Protocol for the determination of methane potential (BMP)

The determination of methane potential involves several steps. Firstly, 500 ml of a solution containing macro and micronutrients is prepared using the chemicals and concentrations mentioned in Tables 1 and 2.

Table.1: Composition of macro-element solution.

Chemicals	Concentration (g/L)
KH_2PO_4	10.00
NH_4Cl	26.60
$CaCl_2.2H_2O$	3.00
$MgCl_2.6H_2O$	6.00
Thioglycolate Na	30.00

Table.2: Composition of micronutrient solution.

Chemicals	Concentration (g/L)
$FeCl_2.4H_2O$	10.00
$CoCl_2.6H_2O$	2.50
$MnCl_2.4H_2O$	0.50
$NiCl_2.6H_2O$	0.50
$ZnCl_2$	0.25
H_3BO_3	0.25
Na_2SeO_3	0.25
$CuCl_2.2H_2O$	0.20
$Na_2MoO_4.2H_2O$	0.05

Regarding the micronutrient solution, all ingredients are dissolved and filtered using a 0.22 µm filter paper and kept at 4°C for further use. A sodium bicarbonate ($NaHCO_3$) buffer solution is prepared by dissolving 50g of $NaHCO_3$ in 1 liter of distilled water. A mass of inoculum corresponding to 100 g of organic matter from a bioreactor specialized in anaerobic digestion of household waste is weighed and mixed with the macro-element (ME) solutions (1.52 ml), micronutrient (OE) solutions (350 µl), and sodium bicarbonate buffer solution (Buffer Vol Sol) (9.10 ml). A mass of the sample (RP) corresponding to 0.8 g is weighed and mixed with the inoculum and the entire solution mixture, and the mixture is added to 250 ml serological bottles. The volume of the liquid phase in all bottles is adjusted to 175 ml with distilled water (Table.3). In the final preparation step, the headspace air of each bottle is purged with a mixture of N_2:CO_2 gas (80:20 v/v) for approximately 1 minute. Subsequently, each bottle is sealed to make it gas-tight by pressure-fitting rubber stoppers and covering them with metal caps. The bottles are placed in an incubator, and mesophilic conditions are maintained throughout the BMP tests, with T° control and oscillatory agitation (35°C, 150 rpm).

To determine methane content (CH_4), the biogas produced in each bottle is monitored by determining the volume (by hydrostatic column) and composition (by GC analysis) on days 1, 3, 7, 13, 21, 27, and 35 [30-32].

Table .3: BMP recipe

BMP bottles	1 à 3	4 à 6	7 à 9
Samples	Inoculum	Starch control	Paper mill sludge
Number	3	3	3
Inoculum quantity (g)	100	100	100
Sample quantity (g)	0	0,35	0,80
Volume of macro-element solution (ml)	1,52	1,52	1,52
Volume of micronutrient solution (µl)	350	350	350
Buffer solution volume (ml)	9,10	9,10	9,10
Volume of distilled water (ml	63,35	63,70	64,50
Total (ml)	175	175	175

3. RESULTS AND DISCUSSIONS

3.1. Characterization

3.1.1. pH

The pH value before and after the anaerobic digestion process decreased from 8.014 to 7.447, indicating that the pH during the process was nearly neutral. This ensures a smooth anaerobic digestion process and prevents inhibition due to acidic conditions, so contributing to the stability of the microorganism's activity responsible for methane production, in conditions where the pH is close to neutral values [33-35].

3.1.2. Total solids (TS) and volatile solids (VS)

The obtained values are provided in Table .4.

Table .4: Total solids (TS) and volatile solids (VS) content.

Sample	Raw powder
Wet sample weight (g) (Before drying)	2,06
Dry sample weight (g) (After drying)	0.96
TS(g/Kg)	467
Ash (g/Kg)	29,75
VS (g/Kg)	437,25

The TS (ashes) of the dried paper mill sludge are estimated at 467 g/kg, and the VS at 437.25 g/kg, which is equivalent to 49% organic matter (Table.4). According to literature, this paper sludge is rich in organic matter compared to other paper sludges [34], making it a potential substrate for the methanization process. Therefore, the organic matter present in the raw powder is 0.4369 g/g.

3.1.3. Ammoniacal nitrogen

The concentration of ammoniacal nitrogen present in the paper sludge before and after anaerobic digestion is estimated at 1375 ppm and 1333 ppm respectively, as shown in the following table. 5.

Table.5: Average concentration of ammoniacal nitrogen before and after the anaerobic digestion process.

Sample	Sample number	Sample mass (g)	Titrant volume (ml)	Ammoniacal nitrogen (ppm)	Average value (ppm)
Mass before process	2	1,94	16,4	1355	1375
		1,99	16,7	1348	
Mass after process	3	1,49	13,5	1343	1333
		1,50	13,3	1307	
		1,51	13,7	1351	

The variation in the concentration of ammoniacal nitrogen is almost insignificant, suggesting a balance between the consumption and production of ammoniacal nitrogen by microorganisms, thus stability of the process, which allows maintaining a balance between different microbial populations [35-36].

3.1.4. Alkalinity

The alkalinity before and after methanization is shown in Table .6.

Table.6: Average values of alkalinity per equivalent of $mgCaCO_3/L$ before and after the anaerobic digestion process.

Sample	Nbr_{sample}	$pH_{initial}$	Vol_{sample} (ml)	Vol titrant (ml)	Average (ml)	Base equivalent $mgCaCO_3/L$
Before methanization		7,6	0,50	5,65		

	2	7,6	0,50	5,58	5,61	7473
After methanization	3	7,5	0,50	5,55	5,49	7276
		7,3	0,50	5,38		
		7,4	0,50	5,55		

According to the results obtained, the alkalinity before and after methanization decreased by 200 eq mg$CaCO_3$/L, which is probably due to acidification of the environment, leading to a decrease in alkalinity in order to achieve a nearly neutral pH during the anaerobic digestion process. This explains the decrease in pH from 8.014 to 7.447.

3.1.5. Organic acids

The table.7 shows the various organic acids present before and after the anaerobic digestion process. The acids present before the process are formic acid (2050 ppm) and butyric acid (1250 ppm). Their presence is due to the paper bleaching process; the use of certain chemicals such as chlorine or hydrogen peroxide can lead to the formation of these two acids as by-products [37]. Formic acid can also be produced by the decomposition of lignin during paper pulp manufacturing [38]. The acid formed after the digestion is propionic acid. Its formation is due to the degradation of amino acids by microorganisms present in the digester (640.5 ppm) [36-39]. The decrease in the concentration of formic acid (120.7 ppm) and butyric acid (680.5 ppm) is due to their consumption by microorganisms to form methane (CH_4) and carbon dioxide (CO_2) [40]. Propionic and butyric acids are considered potential inhibitors for methanogens if their concentrations exceed 2 to 3 g/L [41], which is not the case because their values are below this concentration (0.64 g/L and 0.68 g/L).

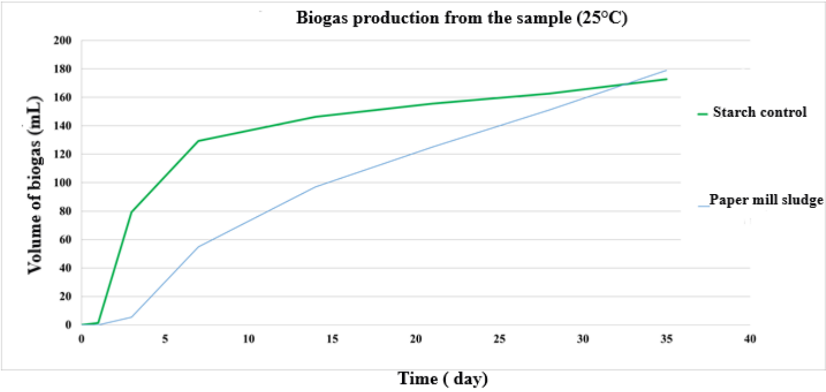
Table .7: Organic acids present in the dried powder before and after methanization.

Sample	Number of samples	formic acid (ppm)	propionic acid (ppm)	butyric acid (ppm)
Initial	3	2050	0	1250
Final	3	120	630	650
		130,7	670	740
		120,4	620	660

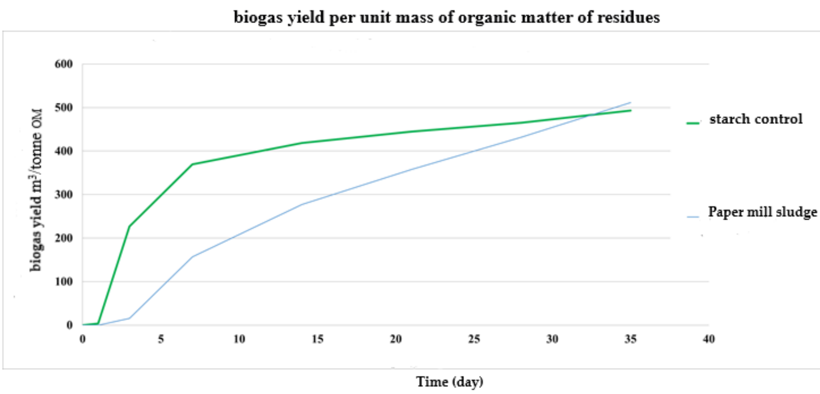
3.2. Anaerobic digestion

3.2.1. Biogas production

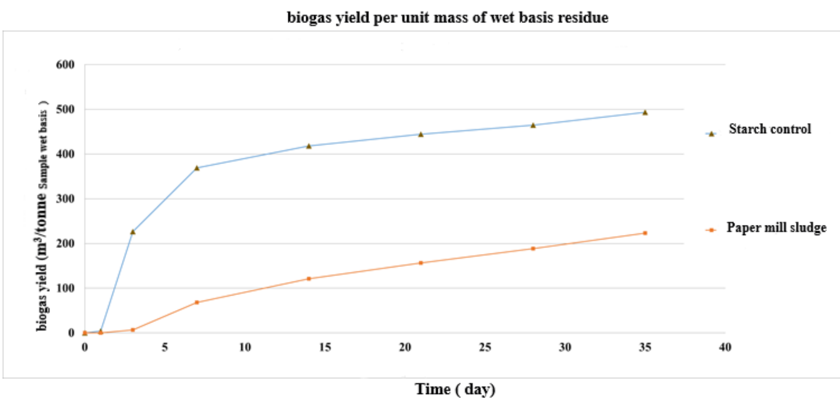
Fig.1 shows the biogas production over time, with an increase observed on the dry basis (Figure.1.a, Figure.2.b) up to a volume of 180 ml and a biogas yield up to 520 m^3/ton $_{OM}$, which exceeds the starch control (reference) on the 35th day (last day) and continues to increase. In contrast, the biogas yield on a wet basis per unit mass of residue is estimated at 200 m^3/tonne $_{\text{Sample wet basis}}$, while the starch control increased up to 480 m^3/tonne $_{\text{Sample wet basis}}$ (Figure.1.c). In a wet-phase anaerobic digestion process, the dry matter content is generally between 10% and 15%, corresponding to 90% to 85% moisture content [42], unlike the dry phase, where the dry matter content is higher (between 25% and 40%) [42]. This means that a larger proportion of the mass consists of solid organic matter. The high biogas production noted in the dry phase is explained by the high dry matter content, which allows better control of nutrients and promotes the activity of microorganisms responsible for the anaerobic digestion [42].



(a)



(b)

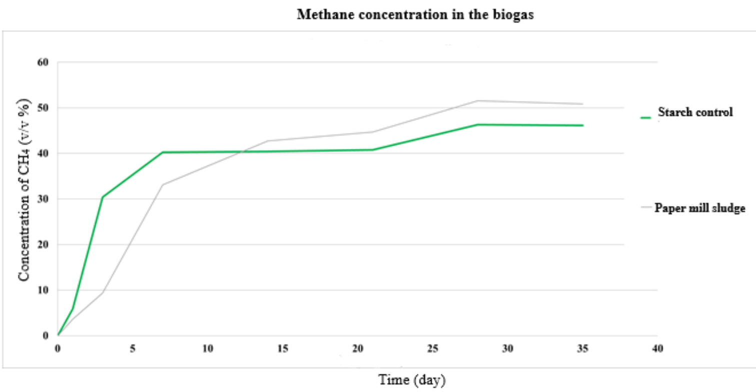


(c)

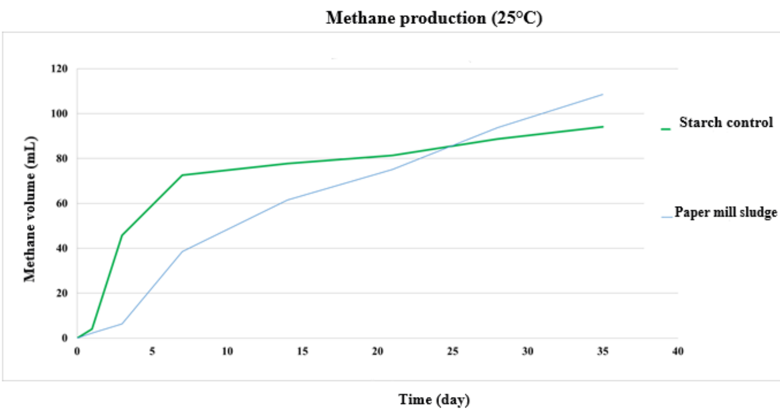
Fig.1 : Biogas production from RP, (a, b) Dry basis; (c) Wet basis.

3.2.2. Methane Production (CH_4)

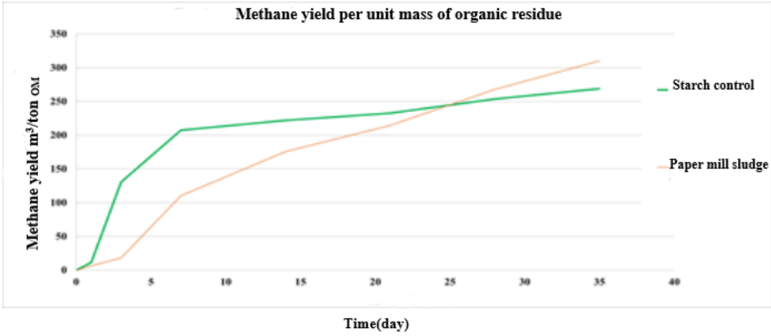
Figure.2 shows methane production over time in two different bases. An increase in methane concentration in the biogas is observed until reaching a plateau on the 28th day with a value of 53% v/v (Figure.2.a), which is higher than the starch control 45% v/v. The plateau obtained is explained by the total degradation of organic matter by microorganisms in the dry base. The volume and yield of CH_4 (Figure.1.b, Figure.1.c) increased rapidly until reaching a value of 110 ml and 320 m^3/ton_{OM} on the 35th day, exceeding the value of the control at 97 ml and 270 m^3/ton_{OM} on the 35th day. However, the methane yield per unit mass of residue in the wet basis is low, with a value of 120 $m^3/tonne_{Sample\ wet\ basis}$ on the 35th day (Figure.2.d), which is half of the value obtained by the starch control at 270 $m^3/tonne_{Sample\ wet\ basis}$ on the 35th day (Figure V.27.d). The low methane yield obtained in the wet phase compared to the dry phase is explained by the higher dry matter content in the dry phase compared to the wet phase [42-43].



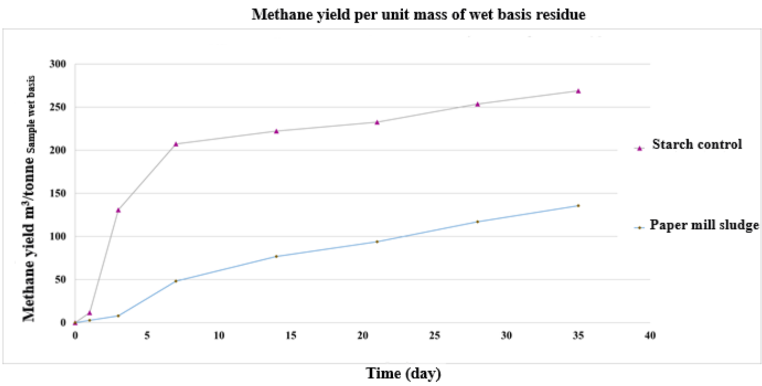
(a)



(b)



(c)



(d)

Fig.2 Methane Production from RP, (a, b, c) dry basis; (d) wet basis.

3.3. Representativeness of this study with other studies on methane production from different substrates

The production of methane has been studied by other substrates, such as orange peel, cereal straw, used grease, sewage treatment grease, mixture of agricultural residues, green leave, potato pulpe and garden waste. The methane production was estimated in the range from 365 (L_{CH4}/Kg_{VS}) for orange peel to 40.8 (L_{CH4}/Kg_{VS}) for garden waste.

The PMS is ranked in 3rd position with an optimal production of 320 (LCH_4/Kg_{VS}), which is very close to that observed for orange peel with a value of 365 (LCH_4/Kg_{VS}), as shown in Table.8. So this residue is estimated to be a potential substrate for the methane production.

Table.8: Methane production by different biomass.

Biomass	Production of CH_4 (L_{CH4}/ KG $_{VS}$)	Reference
Orange peel	365	[13]
Cereal straw	331	[14]
Paper mill sludge	320	This study

Used grease	250	[44]
Sewage treatment grease	240	[44]
Mixture of agricultural residues	239	[45]
Green leaves	55.4	[15]
Potato pulp	50	[44]
garden waste	40.8	[15]

4. Conclusion

Throughout this study, sludge from the paper industry was used as biomass for biogas production through the anaerobic digestion process in two different basis (dry and wet). The biogas production yield is 520 m^3/ton $_{OM}$ in the dry basis and 200 m^3/ton $_{\text{Sample wet basis}}$ in the wet basis. As for the methane yield, the value is 320 m^3/ton $_{OM}$ in the dry basis and 120 m^3/tonne $_{\text{Sample wet basis}}$ in the wet basis.

This study confirms that the PMS from the paper industry can be utilized as a biomass for biogas production, thus providing an eco-friendly and sustainable alternative for the environment.

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References

[1]: D. Pokhrel and T. Viraraghavan, "Treatment of pulp and paper mill wastewater—a review," J. Sci Total Environ., vol. 333, no. 1-3, pp. 37-38, 2004.

[2] :C. Priadin, D. Wulandari, I. Rahmatika, S.S. Moersidik,. "Biogas Production in the Anaerobic Digestion of Paper Sludge", APCBEE Procedia., vol. 9, pp. 65-69, 2014.

[3] : B. Khoury, T. Lecomte, G. Fortin, M. Masse, P. Therien, V. Bouchard, M.A. Chapleau, K. Paquin, S.G. Hofmann, " Mindfulness-based therapy: A comprehensive meta-analysis," Clinic Psych Rev., vol. 33, no. 6, pp. 763-771, 2013.

[4]: T. Kuokkanen, H. Nurmesniemi, R. Pöykiö, K. Kujala, J. Kaakinen, M. Kuokkanen, "Chemical and leaching properties of paper mill sludge, " Chem Spec Bioavailab., vol. 20, no. 2, pp. 111-122, 2008.

[5] :L. Zhang, ChXu and P. Champagne, "Energy recovery from secondary pulp/paper-mill sludge and sewage sludge with supercritical water treatment," Biores Technol., vol. 101, pp. 2713-2721, 2010.

[6] : M. Alkasrawi, A. Al-Othman, M. Tawalbeh, S. Doncan, R. Gurram, E. Singsaas, F. Almomani, S. Al-Asheh S, "A novel technique of paper mill sludge conversion to bioethanol toward sustainable energy production: Effect of fiber recovery on the saccharification hydrolysis and fermentation," Energy., vol. 223, p. 120018, 2021.

[7] : J.J. Camberato, B. Gagnon, D.A. Angers, M.H. Chantigny, W.L. Pan WL, "Pulp and paper mill by-products as soil amendments and plant nutrient sources," Can J Soil Sci., vol. 86, no. 4, pp. 641-653, 2006.

[8] : B. Khoury, T. Lecomte, G. Fortin, M. Masse, P. Therien, V. Bouchard, M.A. Chapleau, K. Paquin, S.

G. Hofmann, “Mindfulness-based therapy: A comprehensive meta-analysis,” Clinic Psych Rev., vol. 33, no. 6, pp. 763-771, 2013.
[9] : L. Zhang, W, Weipu Li, J. Lu, R. Li, Y. Wu, “Production of platform chemical and bio-fuel from paper mill sludge via hydrothermal liquefaction,” J Analyt App Pyrol., vol. 155, p. 105032, 2021.
[10] : M. Merah, C. Boudoukha, A. Avalos Ramirez, M.F. Haroun, S. Maane, “High biosorption of cationic dye onto a novel material based on paper mill sludge,” Sci Rep., vol. 13, no. 1, p. 15926, 2023.
[11] : S. Maane, M. Fodil, M. Merah, A. Avalos Ramirez, M. F. Haroun, “Removal of lead using paper sludge as biosorbent,” Eur Chem Bull., vol. 12, no. 4, pp. 378-390, 2023.
[12]: B. E. Rittmann and P. L McCarty, “Environmental biotechnology: principles and applications,” Tata McGraw-Hill Education, 1st Ed. New York, 2012.
[13] : F. Battista, G. Remelli, S. Zanzoni, D. Bolzonella, “Valorization of Residual Orange Peels: Limonene Recovery, Volatile Fatty Acids, and Biogas Production,” ACS Sustainable Chem Eng., vol. 8, no. 17, pp. 6834-6843, 2020.
[14]: A. Bauer, P. Bösch, A. Friedl, T. Amon, “Analysis of methane potentials of steam-exploded wheat straw and estimation of energy yields of combined ethanol and methane production,” J Biotechnol., vol. 142, no. 1, pp.50-55, 2009.
[15]: L. N. Liew, J. Shi, Y. Li, “Methane production from solid-state anaerobic digestion of lignocellulosic biomass,” Biomass Bioenergy., vol. 46, pp. 125-132, 2012.
[16]: S. Bayr and J. Rintala J, “Thermophilic anaerobic digestion of pulp and paper mill primary 586 sludge and co-digestion of priary and secondary sludge,” Water Res., vol. 46, no. 15, pp. 4713– 4720, 2012.
[17] : 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., vol. 223, pp. 479–486, 2013.
[18]: 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., vol. 298, pp. 162–182, 2016.
[19]: M. Saha, C. Eskicioglu, J. Marin, “Microwave Ultrasonic and chemo-mechanical 595 pretreatments for enhancing methane potential of pulp mill wastewater treatment 596 sludge,” BioresourTechnol., vol. 102, no. 17, pp. 7815–7826, 2011.
[20]: N. Wood, H. Tran H, E. Master, “Pretreatment of pulp mill secondary sludge for high-rate anaerobic conversion to biogas,” BioresourTechnol.,vol. 102, no. 47, pp. 5729–5735, 2009.
[21] : M. Alkasrawi, Z. Al-Hamamre, M. Al-Shannag, M.J. Abedin, E. Singsaas, “Conversion of paper mill residuals to fermentable sugars,” Bioresour., vol. 11, no. 1, pp. 2287-2296, 2006.
[22]: Z. Fan, C. South C, K. Lyford, J. Munsie, P. Van Walsum, L.R. Lynd, “Conversion of paper sludge to ethanol in a semicontinuous solids-fed reactor,” Bioprocess Biosyst Eng., vol. 26, pp. 93-101, 2003.
[23]: S. K. Lister and M. A. Line, “Potential utilisation of sewage sludge and paper mill waste for biosorption of metals from polluted waterways,” Bioresour Technol., vol. 79, no. 1, pp. 35-39, 2001.
[24]: T. Meyer and E.A. Edwards, “Anaerobic digestion of pulp and paper mill wastewater and sludge,” Wat Resear., vol. 65, pp. 321-349, 2014.
[25] : A. A. Wasihun, G. G. Berhe, D. B. Sbhatu, K. H. Abay, G. Gebreyohannes, “Quality Jam from Baobab (Adansonia digitata L) Fruit Pulp Powder: Formulation and Evaluation of Its Physicochemical and Nutritional Properties,” J food Quali., vol. 2023, no. 1, p.8816256, 2023.
[26]: P. L. Kirk , “ Kjeldahl Method for Total Nitrogen,” Anal Chem., vol. 22, no. 2, pp. 354–358, 1950.
[27]: S. Chen, J. Zhang, X. Wang X, “Effects of alkalinity sources on the stability of anaerobic digestion from food waste,”Waste Manag Resear., vol. 33, no. 11, pp. 1033-1040, 2015.
[28]: F. F. Perez and F Fraga, “A precise and rapid analytical procedure for alkalinity determination,” Marine Chem., vol. 21, no. 2, pp. 169-182, 1987.
[29]: M. C. Gancedo and B. S. Luh, “HPLC Analysis of Organic Acids and Sugars in Tomato Juice,” J Food Sci., vol. 51, no. 3, pp. 571-573, 1986.
[30]: C. Holliger, M. Alves, D. Andrade, I. Angelidaki, S. Astals, U. Baier, I. Wierinck, “Towards a standardization of biomethane potential tests,” Water Sci Technol., vol. 74, no. 11, pp. 2515-2522, 2016.
[31]: I. Ingelidaki, M. Alves, D. Bolzonella, L. Borzacconi,, J. L. Campos, A. J. Guwy, J. B. Van Lier.

"Defining the biomethane potentiel (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays," Water Sci Technol, vol. 59, no. 5, pp. 927-934, 2009.

[32]: F. Raposo, R. Borja, C. Ibelli-Bianco, "Predictive regression models for biochemical methane potential tests of biomass samples: Pitfalls and challenges of laboratory measurements," Renewable and Sustainable Energy Reviews., vol. 127, p. 109890, 2020.

[33] : R. Moletta, "Méthanisation de la biomasse," Tech l'ingénieur., pp. 1–21, 2008.

[34] : J. Lindner, S. Zielonka, H. Oechsner, A. Lemmer A , " Effect of different pH-values on process parameters in two-phase anaerobic digestion of high-solid substrates," Envi Technol., vol. 36, no. 2, pp. 198-207, 2015.

[35]: J. J. Lay, Y. Y. Li, T. Noike, "The influence of pH and ammonia concentration on the methane production in high-solids digestion processes," Water Envi Chem., vol. 70, no. 5, pp. 1075-1082, 1998.

[36]: S. Park and M. Kim M, "Effect of ammonia on anaerobic degradation of amino acids," KSCE J Civ Eng., vol. 20, pp. 129–136, 2016.

[37] : E. M. Ekstrand, M. Hedenström, B. H. Svensson, S. S. Yekta, A. Björn, "Methane potentials and organic matter characterization of wood fibres from pulp and paper mills: The influence of raw material, pulping process and bleaching technique," Biomas Bioenerg., vol. 143, p. 105824, 2020.

[38] : M. O. Bengoechean, I. Gandarias, P. L. Arias, T. Barth, "Unraveling the Role of Formic Acid and the Type of Solvent in the Catalytic Conversion of Lignin: A Holistic Approach," Chem Sus Chem., vol. 10, no. 4, pp. 754-766, 2017.

[39] : H. Liu, Y. Chen, J. Ye, H. Xu, Z. Zhu, T. Xu, "Effects of different amino acids and their configurations on methane yield and biotransformation of intermediate metabolites during anaerobic digestion,"J Envi Manag., vol. 296, p. 113152, 2021.

[40] : Y. Wang, Y. Zhang, J. Wang, L. Meng L, "Effects of volatile fatty acid concentrations on methane yield and methanogenic bacteria,"Biomass Bioenerg., vol. 33, no. 5, pp. 848-853, 2009.

[41] : D. Demeyer and V Fievez, "Ruminants et environnement : la méthanogenèse," Animal Resear.,vol. 49, no. 2, pp. 95-112, 2000.

[42]: L. Luning, E. H. M Van Zundert, A. J. F. Brinkmann, "Comparison of dry and wet digestion for solid waste,"Water Sci Technol., vol. 48, no. 4, pp. 15-20, 2003.

[43]: T. F. Carneiro, R. Isaac, M. Perez, C. Schvartz, " Chapter, Biogas Production: Pretreatment Methods in Anaerobic Digestion,"Co-published by Jhon Wiley and sons, Inc. Hoboken, New jersey, and Scrivener Publishing, LLC, Salem, Massachusett. Published simultaneously in Canada, 2012.

[44] : A. Ademe and T. Solagro, "La méthanisation à la ferme," 2006.

[45] : F. Valenti, Y. Zhong, M. Sun, S. M. C. Porto , A. Toscano, B. E. Dale, F. Sibilla, L. Liao L, " Anaerobic co-digestion of multiple agricultural residues to enhance biogas production in southern Italy," Waste manag., vol. 78, pp. 151-157, 2018.