Modeling and Optimization of Chemical Pretreatment for Enhanced Co-Digestion of Paper Sludge

Mansouri Assia[1,*], Bendjaballah-Lalaoui Nadia[1], Berouaken Amine[2], Salmani Rania[1], Boutarka Yousra[1]

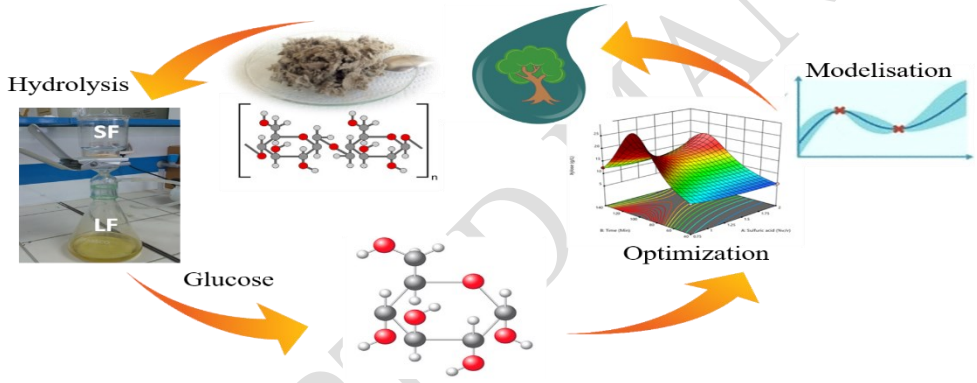
[1]Laboratory of Materials Chemistry, Catalysis, and Environment, University of science and technology Houari Boumediene. U.S.T.H.B, BP 32 El-Alia, Bab-Ezzouar, Algiers

[2]Centre de Développement des Energies Renouvelables, CDER, 16340, Algiers, Algeria.

[*]Corresponding author: Mansouri Assia

E-mail: amansouri@usthb.dz , tel: 213 795 29 12 63

GRAPHICAL ABSTRACT



ABSTRACT

In papermaking industry, large water consumption and hazardous wastes generation, particularly paper sludge, present environmental challenges. This study focuses on the valorization of the paper sludge by optimizing the extraction of total sugars through chemical treatment under various operating conditions. A central composite design was used to investigate treatment conditions, by varying chemical treatment agent (sulfuric acid, H_2SO_4, phosphoric acid, H_3PO_4, sodium hydroxide, NaOH, and hydrogen peroxide, H_2O_2), agent concentration (0.75%, 1.5%, and 2%) and treatment duration (up to 140 minutes). Additionally, experiments were conducted to assess biogas production, with monitoring of key parameters such as cumulative biogas volume, chemical oxygen demand

(COD) and total sugar. Results were analyzed using the modified Seaman model to elucidate chemical treatment reaction mechanisms. Optimal conditions, achieved with 2% (v/v) sulfuric acid treatment at 100°C for 120 minutes, yielded a maximum total sugar concentration of 1738.96 mg/L. These findings demonstrate the potential for efficient utilization of paper sludge for bioconversion into biogas, contributing to sustainable waste management and resource recovery.

Keywords: Chemical treatment, Modeling, Paper sludge, Response surface methodology, optimization, Biogas.

1. Introduction

One of the most taped renewable energy sources, which is also considered to be a promising alternative to fossil fuels, is biomass (Berouaken et al. 2023). Energy production from biomass encompasses the conversion of waste through various techniques, including anaerobic digestion, gasification, pyrolysis, and fermentation (Okedu et al., 2022; Hosseini Koupaie et al., 2019;; Mansouri et al., 2016);. These processes hold promise for substantially reducing waste accumulation and greenhouse gas emissions while concurrently producing renewable energy.

Since the First Industrial Revolution, fossil fuels have continued to dominate global energy consumption, accounting for approximately 81-83% of total energy production as of 2022 (Vinod Vasan, 2024). This dependence has resulted in rising carbon emissions and environmental concerns, necessitating a transition to sustainable energy sources. Biogas is a viable alternative fuel, produced from organic waste through processes such as anaerobic digestion and biomass gasification. It not only offers a higher calorific value than traditional fuels (Al Tanjil, 2019) but also promotes efficient waste management and nutrient recycling. Furthermore, biogas has the potential for generating electricity and heat while significantly reducing greenhouse gas emissions. It can be locally produced from readily available organic materials, supporting decentralized energy systems. Vinod Vasan

(2024) highlighted biogas as an alternative fuel for internal combustion engines (ICEs), emphasizing its benefits in reducing emissions and improving engine performance.

The pulp and paper industry stands as one of the world's largest industries, representing a significant product consumption in many countries (Haile et al. 2021). Nevertheless, this industry generates considerable amounts of solid and liquid waste throughout the paper production process, notably during the washing of wood materials before pulping and the bleaching process. these processes carry significant environmental implications, making environmental intervention a pressing concern(Haile et al. 2021).

Raw materials used in paper manufacturing consist of agricultural residues and forest-based wood (Patel in 2017). These materials are rich in lignocellulose, resulting in primary sludge generated by paper and pulp mills containing substantial organic and water content (Bokhary 2022). Recent advancements in waste treatment and utilization have highlighted the value of paper sludge as a resource for energy production (Tawalbeh et al. 2021). After undergoing treatment to remove residual chemicals, paper sludge can be stabilized for use as a soil amendment or fertilizer. The utilization of paper sludge is highly dependent on its type and composition, which vary significantly based on its source and the manufacturing processes involved. Studies have highlited that the type of paper sludge and its source substrate play a critical role in influencing its biochemical methane potential in biogas production (Gievers et al., 2022). Beyond pretreatment, alternative strategies such as co-digestion with other organic substrates have shown significant promise in enhancing bioenergy yields. Co-digestion provides synergistic effects, optimizing the anaerobic digestion process and boosting methane production. For instance, recent studies on the anaerobic co-digestion of recycled pulp and paper industry waste with vinasse wastewater (Karouach et al., 2021) have demonstrated improved biodegradability of organic waste and enhanced methane yields. This approach offers a viable method for bioenergy recovery and waste valorization in industrial contexts, particularly for facilities handling high organic load effluents, such as those from pulp and paper industries and ethanol distilleries. Additionally, studies by Gievers et al. (2022) further emphasize the effectiveness of co-

digestion, highlighting its potential to integrate paper sludge into bioenergy production systems efficiently.Moreover, paper sludge can be converted into biofuels such as biohydrogen and biodiesel (Venkata Mohan et al., 2016; Cavka & Jönsson, 2013) , bioethanol and biogas (Donkor et al. 2021), with the possibility of production from both pretreated or unpretreated paper sludge (Bayr and Rintala 2012; Veluchamy and Kalamdhad 2017)

Additionally, paper sludge can be utilized in the production of enzyme (Krishna et al., 2014), and bioelectricity (Ketep et al. 2013), or employed in the production of chemicals like xylitol, recognized as one of the top 12 chemicals to be produced in a biorefinery, as endorsed by the US Department of Energy (Vollmer et al. 2022). The valorization of waste from the pulp and paper industry represents a revolutionary and innovative concept for advancing sustainable development(Mandeep et al., 2020), and the use of paper sludge as a bioenergy substrate is an ongoing area of research (Bokhary et al. 2022).

The treatment step is a crucial preliminary stage in the processing of waste for energy production. Its primary objective is to prepare the waste for further processing by eliminating impurities, reducing particle size and recalcitrance, and liberating sugars from the hemicellulosic and cellulosic fractions, or modifying the chemical or physical structure of the feedstock. Although significant progress has been made in the development of new treatment methods, selecting an appropriate one remains a challenge (Vollmer et al. 2022). The specific requirements of the treatment process will vary based on the waste's composition, properties, and the intended end-use application. Notably, despite variation in substrate sources, treatment outcomes remain closely aligned because they all belong to the same family lignocellulosic biomass.

Several treatment methods have been developed to enhance the accessibility of lignocellulosic materials for conversion into value-added products. These methods encompass physical treatment, chemical treatment, combinations of physical and chemical treatment, microbial treatment, enzymatic treatment, and biological hydrolysis of polysaccharides into biologically digestible monosaccharides (Rodriguez et al. 2017) (Haghighi Mood et al. 2013). The primary objective of these treatment

strategies is to increase the surface area available for hydrolysis, dissolve hemicellulose and lignin, and facilitate efficient hydrolysis (Chakraborty et al. 2019b). Among these strategies, chemical treatment using various reagents has emerged as a prominent process and has been extensively tested on numerous lignocellulosic sources. This aim of chemical treatment is to enhance the efficiency of subsequent steps, such as enzymatic hydrolysis or anaerobic digestion, by breaking down the material's structure and improving enzymatic accessibility (Rodriguez et al. 2017).Chemical treatment can modify the functional groups present in paper sludge by breaking down the complex organic compounds into simpler components through chemical reactions. This can involve the addition or removal of functional groups, such as hydroxyl groups, carboxyl groups, or amino groups, from the organic molecules in the paper sludge. For example, acid-based treatment can increase the concentration of carboxyl groups by breaking down ester linkages in the lignocellulosic components of the paper sludge, while alkaline-based treatment can increase the concentration of hydroxyl groups by hydrolyzing the ester linkages (Harmsen et al. 2010).

In the case of paper sludge waste, chemical treatment involves the use of various chemical reagents to enhance treatment efficiency and promote utilization or disposal. The specific process can include acid hydrolysis, alkaline hydrolysis, oxidation, or reduction. Recent studies have shown that acid treatment is a preferred method for processing herbaceous feedstocks, such as corn stover, wheat straw, and switchgrass ((Zhang et al. 2021). Alkaline treatment, on the other hand, has been demonstrated to effectively remove lignin and reduce hydrolysis inhibitors compared to acid treatment (Zhang et al. 2021).

In the realm of chemical treatment, modeling and optimization play crucial roles in reducing the time and cost associated with trial-and-error experimentation while providing valuable insights into the treatment process. Modeling involves the use of mathematical models to simulate and predict the outcome of the chemical treatment. Notably, the literature on kinetic modeling for lignocellulosic treatment remains relatively limited (Hartati et al. 2021). Lignocellulosic biomass, being complex and heterogeneous, poses challenges for modeling. The kinetics of various chemical reactions

involved in lignocellulosic treatment, such as cellulose and hemicellulose hydrolysis, are not fully understood and can vary based on biomass feedstock and treatment conditions. Thus, models are needed to describe the chemical reactions and physical transformations occurring during treatment. Two approaches exist for modeling complex systems: data-driven models and knowledge-driven models. These encompass empirical models, process simulation models, and process kinetic models. Response surface methodology, Gaussian process regression and Mechanistic model are examples (Vollmer et al. 2022).

Optimization, on the other hand, seeks to identify optimal conditions (Mesa et al. 2022), such as reaction time, temperature, and chemical concentration, to achieve desired outcomes. For instance, optimizing acid treatment for paper sludge may involve determining conditions that maximize soluble sugar yield while minimizing the formation of inhibitory compounds affecting subsequent processing. Various optimization techniques exist, including experimental design, response surface methodology (RSM), and artificial intelligence algorithms like genetic algorithms (GA) and artificial neural networks (ANN) (Chohan et al. 2020). The choice of optimization method depends on treatment process requirement and available information. Experimental design, in general, plays a significant role in optimizing chemical treatment by systematically varying process parameters and measuring responses.

In this study, our objective is to find the optimal combination of process parameters to maximizes the desired response. This can be achieved through statistical methods such as Design of Experiments (DOE) and Response Surface Methodology (RSM), which help identify key factors, factor interactions, and ideal operating conditions. After an extensive review of previous research, we have selected the most promising chemical treatment methods for improving total sugar yields from pulp and paper industry waste. The optimal treatment conditions are determined through optimization of the chosen model candidate. Our work goes beyond finding optimal conditions; we aim to develop a predictive model that reduces the need for extensive trial-and-error experiments, ultimately saving time and resources. This model facilitates beter decision-makimg, supports sustainable practices, and

maximizes biogas production, contributing to resource utilization and waste valorization. **2. Materials and methods**

2.1. Source of biomass

Paper sludge (PS) was collected from the effluent of a pulp and paper industry in Algeria. Prior to chemical treatment, the PS was pressed in a filter press to reduce its water content, which was initially around 95%. The pressed PS was then dried at 105°C until a constant weight was reached as indicated in Fig.1. Following drying, the PS was mechanically milled in a mixer to reduce its particle size and was stored in sealed plastic bags until use at 4°C to prevent contamination. The physicochemical characteristics and compositions of the untreated paper sludge are presented in Table 1.

The characteristics of paper sludge may vary depending on its source, but it typically exhibits high contents of cellulose and hemicellulose (Migneault et al. 2010). Additionally, the sludge may contain by-products such as additives (Soucy 2015) and heavy metals used in the manufacturing process, as reported by Zerhouni, (2010). In our study, the primary constituents of the paper sludge were cellulose and hemicellulose, accounting for approximately 43.70% and 40%, respectively. Notably, the cellulose content in paper sludge can vary widely, ranging from 10% to 75% (w/w), as indicated by Donkor et al., (2021) .

The paper sludge exhibited high oxygen and carbon contents, measuring 64000 mg/L chemical oxygen demand (COD) in the elementary analysis.

Table 1. Characteristics of paper sludge.

Parameter	Value
pH	8.01
COD (mg/L)	64000
VFA (mg/L)	220
NH4-N (mg/kg)	440
VS (%TS)	45

TS (%)	39.55
Cellulose (%TS)	43.70

Figure 1. Dried paper sludge.

2.2. Acid, alkaline and oxidative treatment

Paper sludge (PS) underwent pretreatment using acid (H_2SO_4 and H_3PO_4), alkaline (NaOH), and oxidative (H_2O_2) methods. The experimental conditions were selected based on previous research concerning the treatment of lignocellulosic biomass. Paper sludge (PS) was chosen to be pretreated at 100°C.

The treatment procedure involved conducting experiments in in 100 mL flasks, containing 5 g of PS, which were then placed in an oven. PS was subjected to leaching using various chemical reagents, including H_2SO_4, H_3PO_4, NaOH, and H_2O_2, each at different concentrations (0.75%, 1.5%, and 2%). Additionally, two combined treatments were performed: C1 with NaOH-H_3PO_4 and C2 with H_2SO_4-H_2O_2. The selection of combination treatments was based on a study reported by Brummer et al., (2014) and Sun et al., (2016).

After treatment, the bottles were quenched in a water bath at 25°C, filtered using a 0.45 µm pore size filter to obtain the extraction liquor, and the solid fraction was separated and washed several times with distilled water until pH of 7 was achieved. The solid sample was subsequently dried at 105°C in a vacuum oven to a constant weight for FTIR analysis, while the liquid fraction was used for analysis.*2.3. Analytical methods*

The dry matter, volatile solid and total solid content of the paper sludge were determined using standard methods (American Society for Testing and Materials. et al. 2010). The cellulose and hemicellulose content were determined using the Rivers method (Rivers et al. 1983). Analysis of COD, volatile fatty acid (VFA) of the samples followed the procedure outlined by (Baird et al.). The ammonium-nitrogen (NH_4) was measured using Nessler method. To measure the pH, a sample was prepared by mixing 10 g of PS biomass with 100 mL of distilled water.

After the chemical treatment, the samples were centrifuged at 6000 rpm for 10 minutes and then filtred using a vacuum filter with a 0.45 μm membrane filter. Subsequently, they were analyzed using a high-performance liquid chromatography (HPLC) system equipped with a UV-vis detector set to a wavelength of 190 nm. The mobile phase used was acetonitrile-water (75:25, v/v) at a flow rate of 0.6 mL/min, and the oven temperature was maintained at 35 °C. The operation conditions for HPLC analysis can be referred to Jalaludin and Kim, (2021).

The FTIR analysis, the technique was employed to identify the organic functional groups and minerals present in the solid fraction of both treated and untreated paper sludge. The samples were characterized over the range of 4000-400 cm-1. All samples were prepared as sample/KBr pellets at a ratio of 1:100.

2.4. Experimental setup for biogas production

To evaluate the impact of chemical treatment on biogas production, all fractions (solid and liquid) obtained from various pretreatment methods of paper sludge are mixed and then used as substrates for anaerobic digestion, with the pH adjusted to 7. Anaerobic sludge from sewage treatment served as the inoculum, constituting 10% of the working volume. Co-digestion experiments were performed by mixing pretreated and untreated paper sludge at a ratio of 10:90, respectively. The experiments were conducted in 100 mL glass bottles (batch reactor) equipped with caps containing outlets for biogas release at atmospheric pressure. The digestion process was carried out at a temperature of 35°C ± 2°C and an agitation speed of 150 rpm (Zerrouki et al., 2021). Biogas production from the digesters was quantified using the water displacement method (Tamilselvan and Selwynraj, 2024).

3. Kinetic modeling of chemical hydrolysis

During chemical treatment, paper sludge undergoes a transformation where its cellulose and hemicellulose content become solubilized and fractionated into oligosaccharides, monosaccharides, and degradation products (DPs). To gain insight into the reaction mechanisms of each constituent within lignocellulosic biomass and exercise control over the process, researchers commonly employ mass and energy balance models represented by reaction equations (1) to (4), typically using pseudo-first or second-order models. However, creating a comprehensive model is challenging due to variations in reaction mechanisms and the presence of unknown components, which may vary depending on the raw materials and treatment methods employed (Vollmer et al. 2022).

Seaman's model was initially designed to describe wood saccharification using dilute acid, compromising two consecutive first-order reactions. However, this model was found overly too simple in accurately elucidating the hydrolysis mechanism for lignocellulose. Consequently, Tizazu & Moholkar, (2018) introduced a more sophisticated two-phase model, involving rapid and slow reactions. Subsequently, in 2018, Liu et al., (2018) incorporated a ratio parameter, denoted as 'dx', into the reaction process. This parameter represents the degree, signifying the proportion of xylan that undergoes rapid dissolution during the chemical treatment process. In our study, we have adopted and denoted this ratio as "dg" to represent the proportion of glucan dissolution during the chemical treatment process. This degree has been integrated into the reaction process, as illustrated in Fig.2. The kinetic expressions for cellulose hydrolysis are presented in equation 1-3.

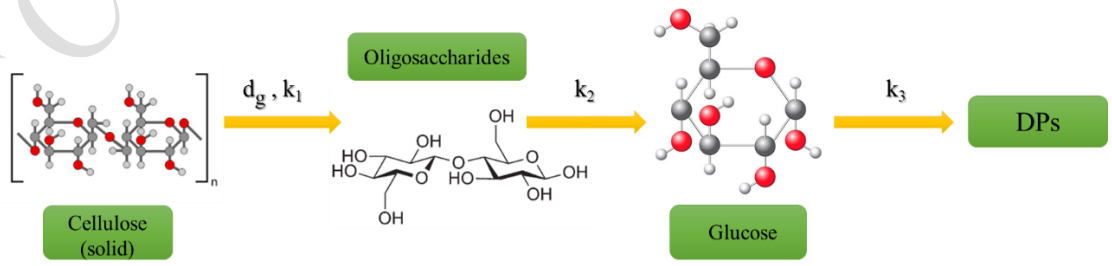


Figure 2. Reaction process for modeling chemical hydrolysis.

$$\frac{dC_G}{dt} = -k_1 C_G \qquad (1)$$

$$\frac{dC_{GO}}{dt} = k_1 C_G - k_2 C_{GO} \quad (2)$$

$$\frac{dC_{GM}}{dt} = k_2 C_{GO} - k_3 C_{GM} \quad (3)$$

Where C_G, C_{GO}, C_{GM} represent the concentration of glucan (G) in the liquid phase (mg/L); glucose oligomers (GO) and glucose monomers (GM), respectively. The rate of glucan hydrolysis is described by k_1, while k_2 and k_3 are the rate constants (min^{-1}) for the second and third reaction steps in Fig. 2.

Considering the initial condition of the reaction, with $C_{GM} = 0$ mg/L and $C_G = d_G\ C_G^0$ at treatment time t=0 min, where d_G represents the glucan dissolution degree. and C_G^0 refers to the initial concentration of glucan in paper sludge without treatment in glucose equivalent (mg/L), and by taking 1.111 in Eq. (5) and (6) which represent the correction factor of conversion of glucan to G oligomers (Olokede et al., 2022), the integration of Eq. (1)-(3) leads to:

$$C_G = d_G C_G^0 \exp(-k_1 t) \quad (4)$$

$$C_{GO} = \frac{1.111 k_1 d_G C_G^0}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \quad (5)$$

$$C_{GM} = \frac{1.111 k_1 k_2 d_G C_G^0}{k_2 - k_1}\left[\frac{\exp(-k_1 t) - \exp(-k_3 t)}{k_3 - k_1} - \frac{\exp(-k_2 t) - \exp(-k_3 t)}{k_3 - k_2}\right] \quad (6)$$

For each chemical treatment (acid, alkali and oxidative), and compounds concentration, we determined the reaction rate constants (k_1, k_2, k_3) and the degree of glucan dissolution (d_G) by fitting experimental data through a least squares algorithm implemented with the MATLAB function lsqcurvefit. The bounds for the kinetic parameters were set within the range of -0.01 and +∞.

4. Optimization of chemical treatment conditions

To optimize the appropriate chemical treatment conditions, we employed a central composite design (CCD) coupled with the desirability function. This design considering the concentration of sulfuric

acid in the range of C = [0.75-2] % (v/v) and the reaction time in the range of t = [0-140] min as variables. C (% v/v) and t (min) were selected as factors for the multiple linear models. Response surface methodology (RSM) was used, which involved fitting a second-order polynomial to the experimental data to predict the optimal conditions for the given set of factors in the design of experiments (Vollmer et al. 2022). The RSM model focused on the predicting the glucose concentration (mg/L) in the liquid phase obtained from the hydrolysis of paper sludge. The operational conditions are outlined in Table 2. The second-order polynomial model (Eq. (8)) used to fit experimental data is as follows:

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ii} X_i^2 + \sum \sum_{j=i+1}^{4} \beta_{ij} X_i X_j \quad (7)$$

$$y = \alpha + \beta \square b + \sum_{i \in D} \gamma_i \square x_i + \sum_{i \in D} \sum_{j \geq i \in D} \delta_{ji} \square x_i \square x_j \quad (8)$$

Where Y is the predicted response, β_0 is a constant coefficient, β_i is the linear coefficient, β_{ii} is the quadratic coefficient, and β_{ij} is the interaction coefficient. The statistical validation was performed by using ANOVA test with a 95% confidence.

Table 2. Rang and level of experimental parameters.

		Ranges and levels				
Variables		-α	-1	0	+1	+α
Product concentration (% v/v)	A	0.49	0.75	1.37	2.00	2.26
Reaction time (min)	B	19.29	40.00	90.00	140.00	160.71

In this study, improving the accuracy of model fitting was achieved through the use of a suitable change of variables. To achieve this, we applied a variance stabilizing transformation, known as the reciprocal (inverse) transformation, as recommended by Mensah et al., (2020). This transformation is illustrated in Eq. (9).

$$y' = (y+k)^{\lambda} \text{ for } |y+k| \rangle 0 \text{ and } \lambda = -1 \quad (9)$$

The optimization was performed using Design expert software, version 13.

5. Results and discussion

5.1. FTIR characterization

The FTIR spectra presented in Fig.3 compare the functional groups present in untreated and treated paper sludge sample. There are similarities in the wavenumbers between the treated and untreated paper sludge. The appearance of -OH groups at 3416 cm^{-1} suggests the presence of functional groups associated with cellulose and hemicellulose in the samples, in accordance with findings by Bokhary et al., (2022). In this study, the moste prominent band was observed at a wavenumber of 3416 cm^{-1} , indicating a high cellulose contain in the paper sludge. The intensity of the absorption peak at 3415 cm-1 increased with higher treatment concentration. Specifically, paper sludge treated with 2% H_2O_2 exhibted the highest intensity at this band, while sludge treated with 2% H_2SO_4 had the lowest intensity 3415 cm-1. This sharper peak at 3415 cm-1 likely indicates the presence of more cristalline cellulose and the disruption of hemicellulose. Furthermore, increased intensity resulting frome H_2O_2 oxydation contributes hydroxyl groups addition (Peretz et al. 2019). Meanwhile, the low cellulose content in paper sludge treated with 2% H_2SO_4 suggests a significant disruption of the crystalline structure, possibly related to the breakage of hydrogen bonds in celllulose hydroxyl groups (Peretz et al. 2019).

The nearby peak at 2914 cm^{-1} , associated with C-H groups, displayed an increase in organic functional band intensity in all treatments except when paper sludge was treated with 2% H_3PO_4, where the band decreased due to organic matter decomposition. A similar observation was reported by Yin et al., (2021) during high temperature pyrolysis treatment of paper sludge.The presence of C = O groups at 1632 cm^{-1} was associated to lactone by Nguyen et al., (2021), while other research linked the functional groups at wavenumber 1635 cm^{-1} to -OH groups (Yin et al. 2021) .Poletto et al., (2013) associated the presence of a peak around 1645 cm^{-1} to water molecules adsorbed on cellulose and hemicelluloses.The peaks at 2361 cm^{-1} , coresponding to symetric C≡C streching, were similar

in untreated and treated paper sludge sample with 1.5% NaOH, 2% H_3PO_4 and 1.5% H_2O_2. However, treatment with 2% H_2SO_4 and 2% H_2O_2 caused a weakenes or even disapearnce of the peak at this peak.

The band at 1429 cm^{-1} was associated to CH_2 from carbohydrates, And this peak notably decreased after treatment with 2% H_2SO_4, possibly due to the dissolution of cellulose and hemicellulose in the liquid fraction. Meanwhile, the band position at 1160 cm^{-1} asscіated to C-O-C streching showed a significant drop compared to other treatments. As noted byTawalbeh et al., (2021), this band was associated with the presence of glucosidic bonds of carbohydrates contirbuted by cellulose. Notably, tretament using 2 % of sulfiric acid exhibited a high intensity at this band, indicating that the composition of sludge after acid treatment is rich in carbohydrates.

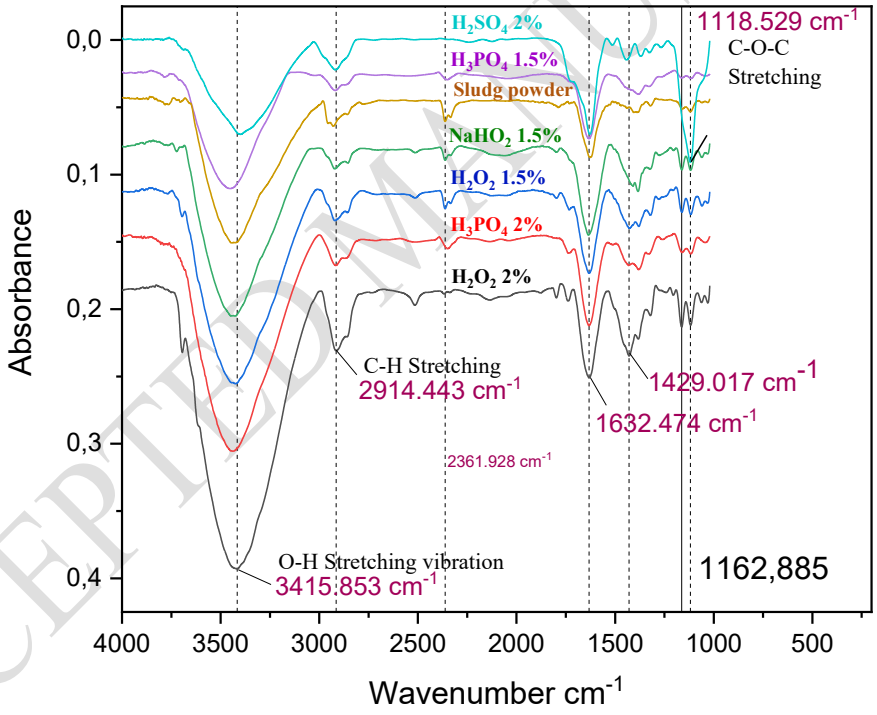


Figure 3. Fourier transform infrared spectroscopy spectra of raw paper sludge sample and paper sludge samples after various pre-treatment.

5.2. Chemicals treatment

Fig. 4 illustrates the effect of various chemical treatments on paper sludge. The highest glucose concentration reached 1738.961 mg/L after of treatment with 2% H_2SO_4, as depicted in Fig. 4. prolonging the treatment duration and increasing H_2SO_4 concentration enhanced glucose yield, this

finding are in line with those noted by Mensah et al., (2020). A significant amount of H_2SO_4 plays an important effect in breaking down cellulose bonds, even in the presence of crystallinity, resulting in increased sugar yield. Dilute sulfuric acid enhances glucose yield, due to the high cellulose content in paper sludge.

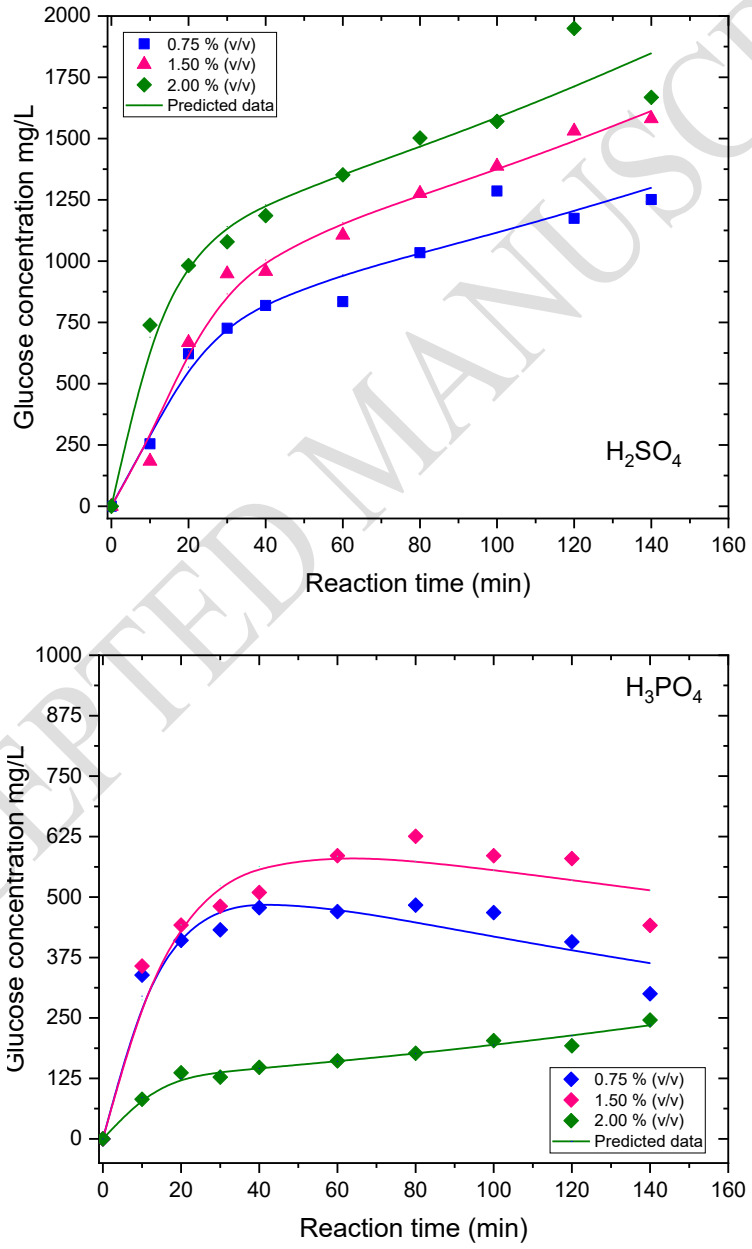
Hydrolysis with 2% H_3PO_4 yielded a maximum glucose concentration of 867 mg/L. After 60 minutes of hydrolysis with 1.5% and 0.75% of H_3PO_4, the cellulose saturation led to declining glucose concentration, indicating acidic environments can cause glucose degradation. NaOH hydrolysis under 1.5% (v/v) and 2% (v/v) concentration increased extracted glucose, reaching a plateau at approximately 80-140 minutes, where glucose concentration remained nearly constant. Similar trends were observed for ethanol based auto-catalyzed organosolv (EACO) pretreatment (Liu et al. 2018), hot water, and dilute acid treatment.

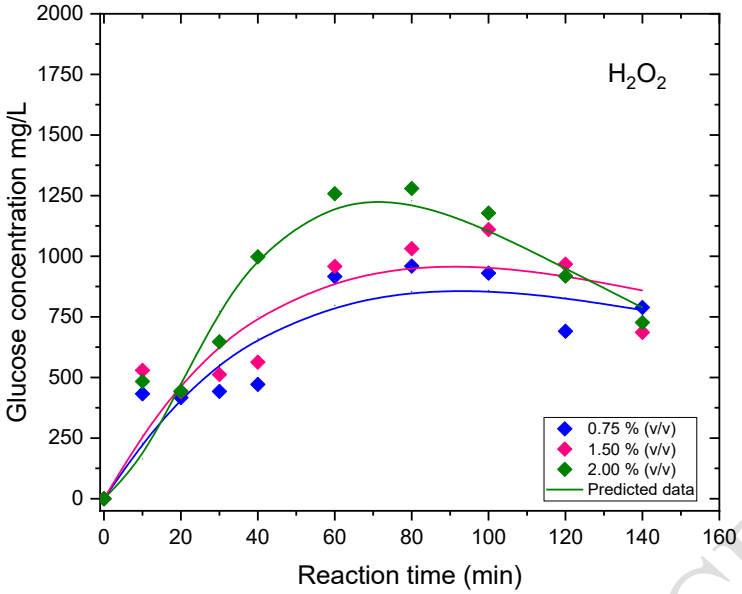
In the case of H_2O_2 treatment, hydrolysis at 100°C for 140 minutes gradually increased glucose concentration for all chemical concentrations, reaching a maximum and remaining stable within the 60 - 80 minutes interval. Beyond 80 minutes, sugar concentration decreased, possibly due to glucose dehydratation into 5-hydroxymethylfurfural, HMF (Menegazzo et al. 2018), or glucose isomerization into fructose in the presence of H_2O_2 (Takagaki et al. 2021). These results suggest that H_2O_2 alone may not be sufficient for glucan degradation, or it could have reacted with cellulose.

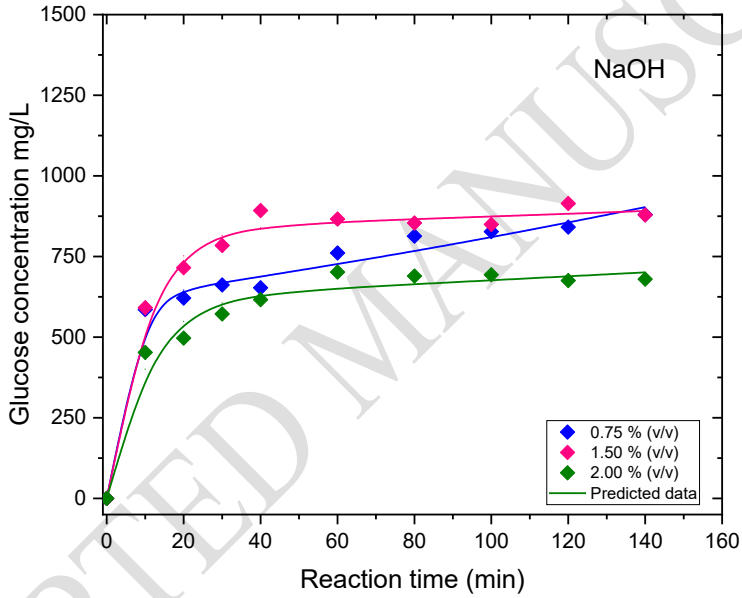
5.3. Kinetics models for chemicals treatment

Cellulose hydrolysis kinetics were conducted at various treatment concentrations of (0.75%, 1.5%, and 2%), as depicted in Fig.4. Table 3 provides insight into the degree of dissolution, reaction rate constants (d_G and k_i), and the root mean square error (RMSE). The analysis revealed that treatment with acid, NaOH, and combined treatments initially increased glucose concentration, reaching a peak of 1257.79 mg/L for paper sludge treated with 2% (v/v) H_2O_2 and 625.65 mg/L for 1.5 %(v/v) H_3PO_4, after 80 minutes. subsequently, glucose concentration gradually decreased, consistent with the proposed reaction Fig.2, where glucose oligomers act as intermediates

Table 3 highlights the strong correlation between experimental and modeled results, confirming the validity of the proposed rate law. The model adapted from Liu et al., (2018), effectively describes glucan hydrolysis in all investigated treatment cases. Notably, the rate constant for oligomer formation (k_1) is higher than that of glucose degradation, indicating that cellulose hydrolysis into oligomers predominates in this treatment process (Becker et al. 2021). For H_2O_2 treatment, k_3 exhibits a value of approximately 0.01, signifying degradation resulting in declining glucose concentration beyond 80 minutes of reaction time.







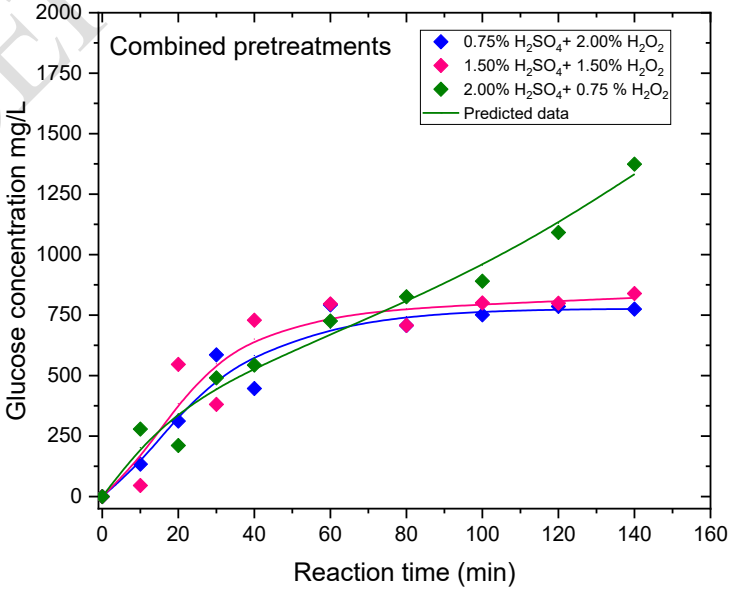


Figure 4. Modeled and measured glucose formation during several chemical treatment**.**

Table 3. Kinetics model parameters for glucan dissolution during chemical treatment.

Reagent treatment				H_2SO_4		
	k_1	k_2	k_3	dg	R^2	RMSE
0.75%	0.2492	0.0717	-0.0038	0.3598	0.9698	69.7014
1.5%	0.1039	0.1039	-0.0040	0.4377	0.9604	50.2097
2%	NA	0.0906	-0.0031	0.5068	0.9945	38.8937
Reagent treatment				H_3PO_4		
	k_1	k_2	k_3	dg	R^2	RMSE
0.75%	NA	0.0755	0.0035	0.2501	0.9379	34.6208
1.5%	NA	0.0581	0.0020	0.2906	0.9317	45.1136
2%	0.2280	0.2280	-0.0048	0.0553	0.9788	09.4727
Reagent treatment				H_2O_2		
	k_1	k_2	k_3	dg	R^2	RMSE
0.75%	NA	0.0113	0.01060	0.9999	0.8357	117.8363
1.5%	NA	0.0130	0.00960	0.9999	0.8244	135.9346
2%	0.0450	0.0450	0.01130	0.9998	0.9141	114.6408
Reagent treatment				NaOH		
	k_1	k_2	k_3	dg	R^2	RMSE
0.75%	NA	0.2462	-0.00270	0.2743	0.9892	25.1507
1.5%	NA	0.1118	-0.00004	0.3682	0.9885	28.0397
2%	NA	0.1018	-0.00008	0.2747	0.9737	33.0546
Reagent treatment				Combined		
	k_1	k_2	k_3	dg	R^2	RMSE
0.75%	0.1577	0.0416	0	0.3462	0.9466	64.1007
1.5%	0.0855	0.0855	-0.00008	0.3292	0.9103	90.2886

2%	NA	0.0504	-0.00820	0.2158	0.9774	60.2637

5.4. Response surface of glucose yield

The experimental design was applied to identify the variables affecting paper sludge treatment and their impact on glucose content. Quadratic polynomial models were employed to fit the experimental data, which were subsequently validated through an analysis of variance (ANOVA) test. Fig. 5 illustrates the interactive effects of process parameters, specifically reaction time and reagent concentration, on glucose yield. the results clearly demonstrate the significance of reaction time and glucan dissolution (P-value = 0.001). Among the various treatment methods, sulfuric acid treatment consistently yielded higher glucose content compared to other chemical reagents. Glucose yields ranged from 73.59% to 98.13% with reagent concentrations ranging from 0.75% to 2% and reaction times between 120 to 140 minutes. It's evident that longer reaction times and higher reagent concentrations led to increased glucose concentration.

The contour plot presented in Fig. 6 illustrates the relationship among glucose concentration, reaction time, and H_2SO_4 concentration. The plots demonstrate that higher glucose concentrations are achieved when treatment conditions exceed 1.25 % H_2SO_4 and a reaction time of 100 minutes. Extending the reaction time to 120 minutes further enhances glucose formation and cellulose dissolution with 1.5% H_2SO_4. These findings align with those of Mensah et al., (2020), who observed a 66% hemicellulose dissolution after 3.5 hours of treatment at 100°C. The contour plot validates the kinetic model and the response surface methodology (RSM) model, indicating that RSM can effectively predict optimal conditions, including higher temperatures, moderate reaction times, and lower acid concentrations, as suggested by Vollmer et al., (2022).The model's adequacy was assessed using ANOVA (Table. 4), where the p-value of 0.0007 suggests the significance of all model terms. The sum of squares and mean square value of 0.1273 for all residuals from the ANOVA demonstrates the close agreement and low noise level between the predicted and actual glucose concentration. Additionally, the coefficient of determination (R^2) for the regression was determined to be 99.97%,

indicating a satisfactory regression for model development. Furthermore, the validation plot (Predicted against Actual) highlights minimal differences (disparities) between predicted responses and experimental values.

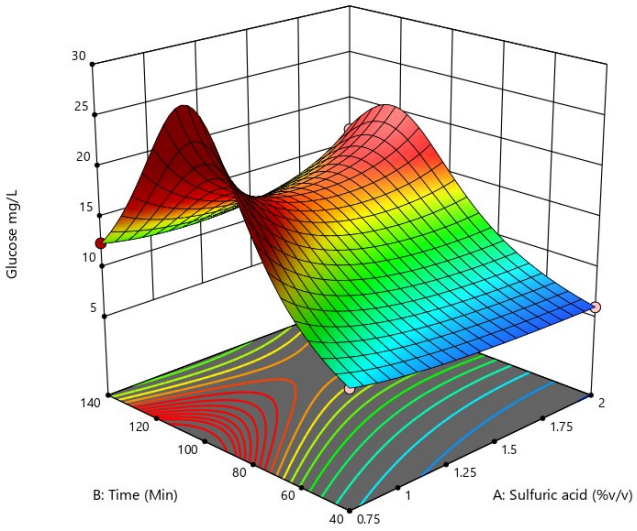


Figure 5. 3D surface plots for interactive effect of sulfuric acid concentration and reaction time.

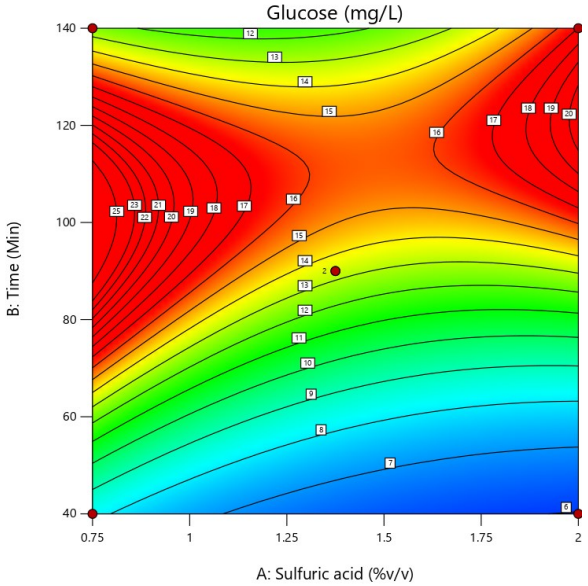


Figure 6. Contour plot of released glucose from treatment of paper sludge hydrolysis versus sulfuric acid (A) and time (B).

Table 4. Analysis of variance for the used model.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	0.1273	5	0.0255	1350.37	0.0007

A-A	0.0035	1	0.0035	186.48	0.0053
B-B	0.0350	1	0.0350	1856.80	0.0005
AB	0.0081	1	0.0081	427.67	0.0023
A^2	0.0018	1	0.0018	95.31	0.0103
B^2	0.0307	1	0.0307	1625.39	0.0006
Residual	0.0000	2	0.0000		
Lack of Fit	0.0000	1	0.0000		
Pure Error	0.0000	1	0.0000		
Cor Total	0.1274	7			

5.5. COD, VS, VFA and ALK variation from inital to final anaerobic digesters

The Chemical Oxygen Demand (COD) before methanation is 64,000 mg/L, which decreases significantly to 9,410 mg/L, representing an 85.3% reduction Table 5. These COD results confirm the high biodegradability of the organic matter in the sludge and the effective performance of the anaerobic digester. The VFA/ALK ratio is an important factor that influences biogas production variability. A ratio below 0.5 greatly supports anaerobic digestion and, consequently, methane production. In our case, the VFA/ALK ratio remains below 0.5 at both the beginning and end of the methanation process

Table 5. Initial and final values of key parameters during anaerobic digestion

	Initial	**Final**
VS (%TS)	45	20
COD (mg/L)	64000	9410
VFA (mg/L)	220	450
ALK (mg/L)	3400	1700
Rapport (VFA/ALK)	0.064	0.26

5.6. Biogas production in the anaerobic digesters

In all bioreactors, the volume of biogas produced increases continuously, indicating effective digestion. Both reactors displayed rapid degradability, which may be attributed to the presence of non-specific microbial populations from the untreated inoculum, as observed by Dahiya et al., (2022) and cited in (Tampio et al., 2019). This could also be linked to the relatively small working volume of 100 mL in this study.

In the first reactor containing untreated paper sludge, biogas production begins after 6 hours of reaction, with an initial volume of 6.24 mL/L g VS. A gradual increase is observed over time, reaching a maximum of 32.58 mL/L g VS after 104 hours (6 days) of retention time. This slow increase reflects the limited availability of easily degradable organic matter in untreated paper sludge.

In the second reactor, which involves co-digestion of untreated and pretreated paper sludge (Figure 7b), a significant increase in biogas production is observed. Initially, biogas production remains low for the first two days, followed by a rapid increase starting on the third day. By the sixth day (150 hours), the maximum biogas production reaches approximately 705.99 mL/L g VS. This higher biogas output suggests the positive effect of pretreatment, which enhances the biodegradability of paper sludge by breaking down complex organic matter into simpler, more accessible substrates for microbial activity. The enhancement of biogas production due to pretreatment has been reported by Zerrouki et al. (2021), who investigated ultrasound pretreatment as a technique to solubilize organic matter and ferment fruit juice wastewater in an anaerobic batch reactor. In their study, biogas production increased from 162 NmL biogas/g VS to approximately 409 NmL biogas/g VS.

Additionally, Banu et al. (2023) observed a biogas production of 174.3 mL/g COD when using pretreated sludge, compared to 52 mL/g COD in the control sludge. This further supports the notion that pretreatment, by enhancing the presence of easily biodegradable organic matter, can improve microbial conversion into biogas.

The data also reveal two peak phases of biogas production, characterized by initial increases followed by a steady production level. This pattern suggests that microbial activity stabilized after the initial

peaks, indicating a balance between organic load and microbial capacity. These results imply strong microbial activity in the reactors, supported by the sufficient availability of easily degradable organic material, which facilitated efficient biogas conversion.

Moreover, the pH values measured after digestion (Table 6) provide further support. For untreated paper sludge, the final pH was 6.48, indicating limited acidification during the process. In contrast, the pretreated paper sludge exhibited a lower final pH of 4.84, consistent with the production of acidic intermediates during anaerobic digestion. This pH drop suggests higher microbial activity and more efficient degradation of organic matter in the pretreated sample, which aligns with the significantly higher biogas yield observed.

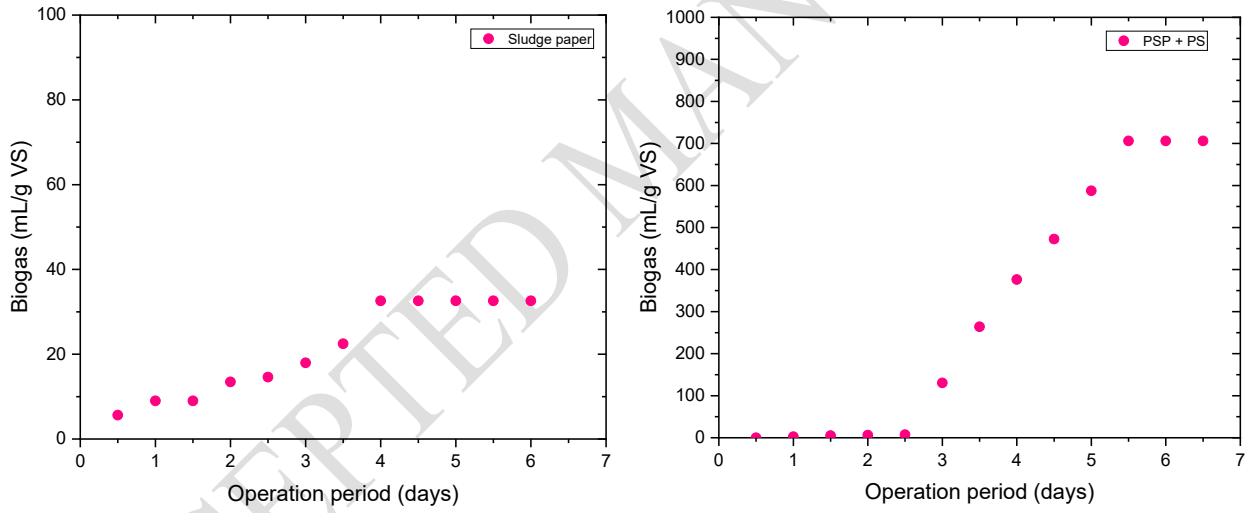


Figure 7. Daily variation of biogas production (a) fisrt degester with paper sludge, (b) second degester (co-digestion of Paper sludge pretreted + Paper sludge)

Table 6. initial and final values of pH before and after anaerobic digestion

Trial	pH before digestion	pH after digestion
Untreated paper sludge	7.00	6.46
Treated Paper Sludge	7.00	4.84

6. Conclusion

The experimental design and analysis of glucan hydrolysis kinetics in the pretreatment of paper sludge have provided valuable insights into the factors affecting glucose content. Our experimental data have been successfully validated using the modified Seaman model and quadratic polynomial models, leading to the identification of significant variables. Among these, reaction time has emerged as a key factor influencing glucose formation. Notably, sulfuric acid pretreatment has shown a significant effect, consistently yielding higher glucose yields compared to the other chemical reagents investigated. Furthermore, the contour plot analysis has confirmed that extended reaction times and increased reagent concentrations significantly promote glucose formation and cellulose dissolution.

In addition, the biogas production results highlight the efficiency of the anaerobic digestion system. The consistent increase in biogas yield, coupled with the observed reduction in organic parameters, underscores the potential of effectively utilizing pretreated paper sludge for sustainable biogas production.

These findings demonstrate that the pretreatment of paper sludge can enhance both glucose production and biogas generation, making it a promising approach for waste to energy applications. The study provides critical insight for determing the optimal parameter for paper sludge pretreatment, with the dual goals of maximizing glucose production and enhancing biogas yields. This integrated approach not only supports waste reduction in the paper industry but also facilitates the efficient utilization of biomass resources in biorefineries, promoting a more sustainable circular economy in waste management and bioenergy production.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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