

Effect of EDTA Treatment on Fiber Structure of Banana Stem

Hafidah Binti Lapok, PM Dr Junaidah Jai, and Nurul Amal Nadhirah

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract— In order to increase the efficiency of pulping, pre-treatment methods were introduced which is known as EDTA (Ethyldiaminetetraacetic acid) that act as chelator to remove the lignin and hemicellulose partially before it undergoes the pulping process. This study was conducted to study the effect of EDTA on cellulose structure and lignin removal rate during soda pulping of banana stem. The pulping process was conducted under atmospheric pressure using NaOH (Sodium hydroxide) at 20% wt/vol and Liquor: Solid ratio of 10. EDTA was added at various concentration (0, 5, and 10%) and the pulping time was carried out for 60, 90 and 120 minutes for each sample respectively. In this study, the banana stem was characterized for yield, kappa number, microscopic viewing and TGA. It was found that the soda pulping process with 20% NaOH, 10% EDTA, and cooking time 60 min showed the best result where the optimum conditions were defined. The experimental values and other studies values was observed in order to get the accurate result.

Keywords— *Banana stem, cellulose, EDTA pre-treatment, hemicellulose, lignin, paper, soda pulping.*

I. INTRODUCTION

In recent years, the use of wood in pulp and paper making has increased due to population growth and constantly rising demand for paper, which has resulted in environmental impacts on the global climate. To reduce the wood consumption, some researchers change the raw material for pulp and paper to renewable lignocellulosic material. Annual plants could be the new sources of lignocellulosic fibres for pulp and paper industry.

Banana crop which is from agricultural residues generates large amount of post-harvest wastes [1]. Agricultural residues offered several advantages where these raw materials can be produced annually and have lower lignin contents compared to wood. Furthermore, they also can be delignified easily which it can be cooked faster and required mild conditions which is it does not need high temperature and longer time for cooking process comparing with wood fiber sources [2].

These recent years have seen the pulping industry utilizing mechanical or chemical processes to extract lignocellulosic plant fibers. Commonly, pulping use chemical reactants to dissolve the composition of lignocellulose in raw materials, while mechanical pulping use refining or grinding methods to separate the raw material into fibrous material and there is also semi-chemical process used. In this research, soda pulping is chosen as it is contribute to higher paper strength produced and it has simplest process that has been applied to various type of non-wood materials such as Tunisian vine stem [3], rice straw and EFB [4].

Chemical pulping provides a lot of bad effects to the environment because of the wastewater pollution. Furthermore, chemical used in the production of pulp and paper also can generate a lot of chemical waste after processing and it must be

treated before being released back to the environmental. Besides, the major drawback of using soda pulping is it used high temperature of cooking temperature where high energy consumption is needed.

In this research, the chemical used as pre-treatment is Ethylenediaminetetraacetic acid (EDTA) where it produced organic chelators. Chelator agents is normally used in pulp and paper industry to improve the process efficiency. Chelator agents used to bind the different metal ions with different charges where it prevent the metal ions to form with other undesired complexes or catalysing undesired chemical reactions [5].

According to study conducted by Ainun et al., (2018a), pre-treatment might decrease the cellulose crystallinity, thus it can increase the porosity of accessible surface area of lignocellulosic materials and also to remove the lignin and hemicellulose partially before it undergoes the pulping process.

Hence, the objectives of the present work are to analyze the effect of EDTA pre-treatment on the cellulose structure of banana pulp during atmospheric soda pulping process. To achieve the objective, characterization of banana stem using microscopic viewing, FTIR and TGA was done where it is the most opportune approach.

II. METHODOLOGY

A. Raw material and preparations of samples

Banana stem (*Musa paradisiaca*) was collected from the residents in Seksyen 7, Shah Alam. The foliage was separated and cleaned with the tap water. Then, the samples parts were cut into chips of 3×3 cm, and dried in oven at 105°C. The preparation of samples was using method of TAPPI T 264 om-88 where the chips of banana stem were grinding, and it will completely remove its moisture content using 400 µm sieved to pass for further used in the pulping process.

B. Pulping Process

Soda pulping was used to separate the cellulose in banana stem from other fibre structure such as hemicellulose and lignin. A chemical pre-treatment was done by dissolved the banana stem in alkaline cooking liquors which is based on sodium hydroxide solution and EDTA. The effect of the following parameters: (i) Liquor to solid ratio: 10:1; (ii) NaOH: 20 wt%; (iii) EDTA: 0, 5, 10 wt%; (iv) Cooking temperature: boiling (~110°C); (v) Pulping time: 60, 90, 120 mins were studied.

C. Pulp characterization

i. Yield

Yield was done after the cooking process to get the pulp yield. The fibre sample need to be grinding to separate the fibre from the banana stem. Then, followed by the extraction of soluble in cooking process with NaOH. The residue from the cooking process

was expressed as a proportion of fry weight of the original sample which is known as pulp yield.

ii. Kappa Number

In this method, 0.1N of potassium permanganate solution was used with one gram of moisture free pulp under specific conditions. Firstly, disintegrate the sample in reaction beaker and make sure the temperature in the reaction beaker constant at 25°C. Then, the suspension is continuously stirred to produce a vortex about 25mm deep. Potassium permanganate solution and sulfuric acid solution was added into the disintegrated sample simultaneously. After 10 minutes, stop the reaction and added potassium iodide solution then after all the solution was mixed, immediately titrate the free iodine with the sodium thiosulfate solution without filtering out the fiber sample. Then, few drops of starch indicator were added at the end of the reaction.

iii. FTIR

FTIR (Fourier Transform Infrared Spectroscopy) was used to access the crystallinity index of the fiber. Pulp sample were crushed to form a very fine powder and then compressed into thin pellet for analysis. The range for spectral scanning was done at 500-4000 cm^{-1} .

iv. Microscopic Imaging

The morphological properties of the pulp fibre was done under microscope at different magnifications. The slide preparation was done by dilute each sample with distilled water to disintegrate the fibre free from bundles then dried in the oven for a few minutes.

v. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was done to approximate the weight loss with respect to temperature due to the release of moisture and volatile matter. In this research, TGA were carried out with 20g of sample was taken and the experiments were conducted in a temperature range of 25 to 900°C with the heating rate of 10°C/min.

III. RESULTS AND DISCUSSION

A. Chemical characterization

Table 1: Preliminary experimental data on Soda pulping of banana stem

Pulping time (min)	EDTA charge	Yield (%)
60	0	22
	5	25
	10	30
90	0	18
	5	18
	10	29
120	0	14
	5	14
	10	17

Cooking conditions: 20% of NaOH, L:S is 10, heating at boiling temperature and atmospheric pressure.

Soda pulping of banana stem was carried out with varying cooking time and EDTA charge at boiling temperature as shown in Table 1. Based on Table 1, the presence of EDTA in the pulping process has attributed to a slight increase in cellulose yield. The greater the addition of EDTA in the soda pulping process, the higher the increase of cellulose yield where the EDTA acts as antioxidant protecting the cellulose against the degradation of NaOH on hemicellulose and cellulose in fibers [7]. Pulp yield decreased with the increasing of EDTA charge from 22% to 17%. The maximum cooking time of 60 minutes was found to produce maximum pulp yield. With respect to pulp yield, the obtained pulp using 5% EDTA and 60 minutes cooking may be considered as

optimum cooking condition to determine the kappa number. As a result, kappa number is 43.

B. FT-IR

FTIR analysis was performed to determine the functional groups on treated banana stem which are shown in Figs 1-3. The peaks region at 3500-2500 cm^{-1} is related to OH and CH₂ groups where the 3300 cm^{-1} band was decreased due to the removal of the hemicellulose component [8]. From Fig 1, 0% EDTA has the highest absorbance of hemicellulose component. 5 and 10 % of EDTA addition to the soda pulping have almost the same peak region where the absorbance of hemicellulose component is much the same. Based on Fig 2, similar peak of the absorbance of hemicellulose component is observed while on Fig 3, 5% of EDTA have the lowest absorbance compared to 0 and 10% of EDTA in the pulping process.

The peaks located at 2900 cm^{-1} is attributed to CH groups which is represent as aliphatic groups in FTIR. In this bands, lignin from treated banana stem has the highest intensity. Compared to the three figs below, 60 minutes of cooking time has the highest absorbance band which attributed to the lignin. The absorbance of peaks at region 1700- 1750 cm^{-1} is assigned to the carbynic stretch vibration which it is strongly depending on the lignin studied. Fig 2 and 3 shows similar peak absorbance while in Fig 1, 0% of EDTA has the highest frequency compared to the 5 and 10% of EDTA.

It is observed that there are peaks around 1200 cm^{-1} which related to the CO and C=C stretching. This peak depicts the typical structure of cellulose. The peak of 895 cm^{-1} is related the rotation of glucose residue around the glucosidic band because it is important to analyze the changes of cellulose occurring during the treatment of banana fibers. These range of absorbance shows sharp and intense peaks which attributed to the cellulose fibers. compared to all three figs, 60 minutes of cooking time has the best peak.

From the discussion above, 60 minutes shows the best result which can be confirmed from the yield obtained in Table 1 where 60 minutes has the highest pulp yield among the 90 and 120 minutes of cooking time.

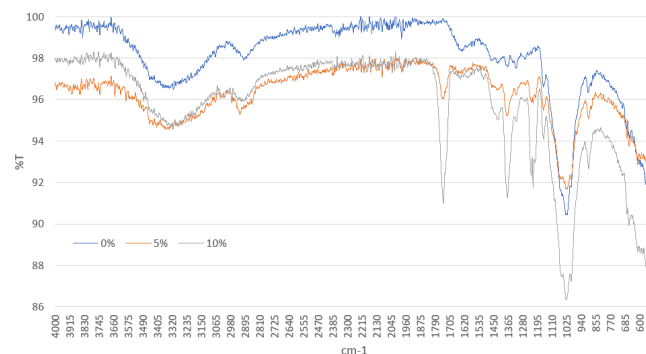


Fig 1 FTIR of banana stem at 60 min of cooking time. Blue: 0% EDTA, Orange: 5% EDTA, Gray: 10% EDTA

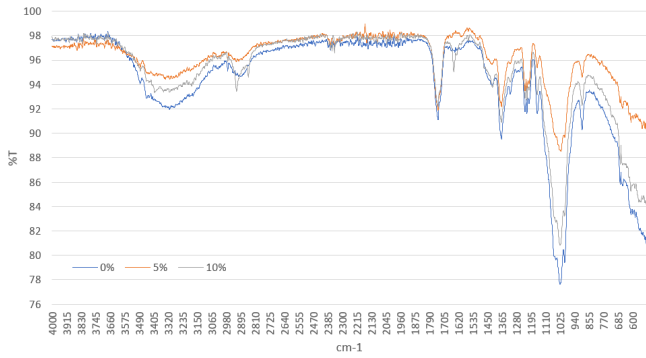


Fig 2 FTIR of banana stem at 90 min of cooking time Blue: 0% EDTA, Orange: 5% EDTA, Gray: 10% EDTA

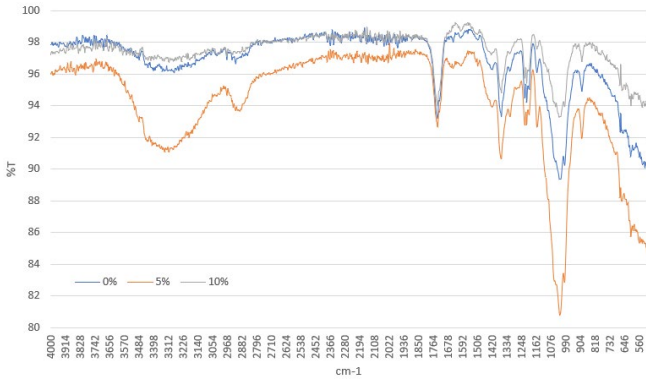


Fig 3 FTIR of banana stem at 120 min of cooking time. Blue: 0% EDTA, Orange: 5% EDTA, Gray: 10% EDTA

C. Microscopic Viewing

The surface morphology of banana stem was observed by using microscope viewing. The microscopic morphological of soda pulping samples was done under 4x and 10x magnification to observe the presence of fibrous after soda pulping process. The presence of fibrous can be clearly seen from Figs 4-6. The fibers are usually thick and thin wall. The fibers of pulp sample are longer than hardwoods. The walls of fiber are smooth, and the diameter of the fibers shows little variation. A higher fiber length of pulp sample showed higher tearing strength of paper. From the figure, 60 minutes of cooking time has the fibrous fiber among the pulp sample.

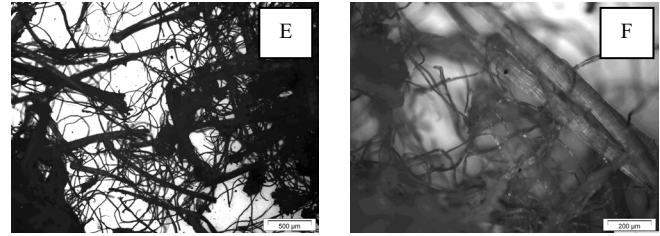
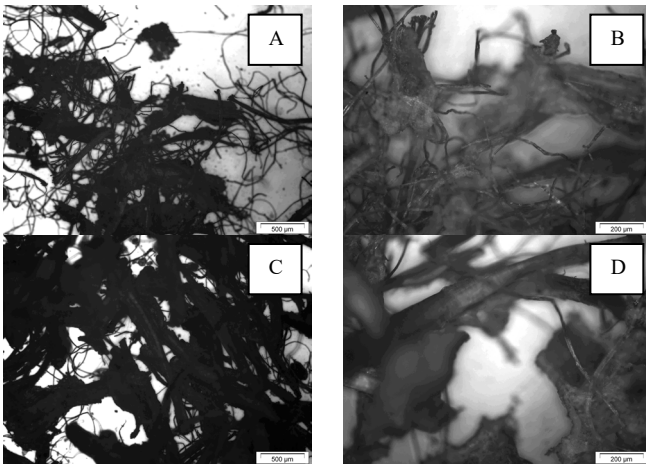


Fig 4 Microscopic morphology for banana fiber cooked at 60 minutes. A) 0% EDTA under 4x magnified, B) 0% EDTA under 10x magnified, C) 5% EDTA under 4x magnified, D) 5% EDTA under 10x magnified, E) 10% EDTA under 4x magnified, F) 10% EDTA under 10x magnified

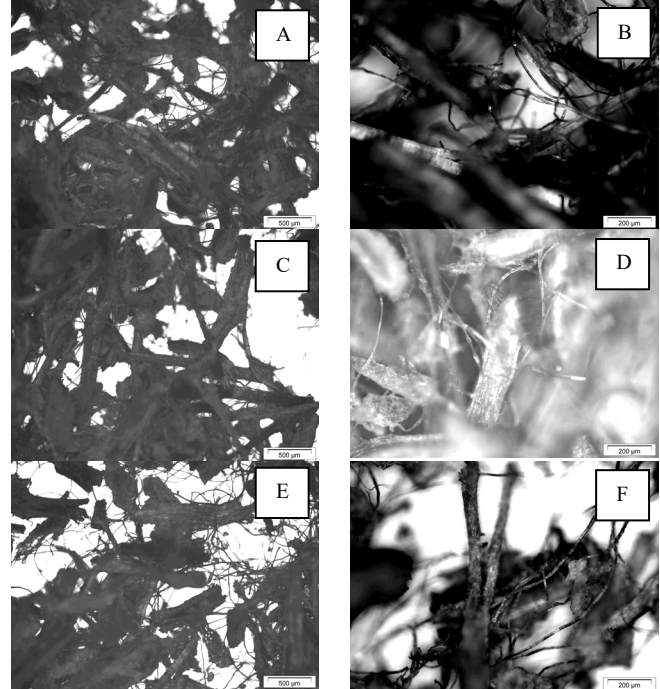


Fig 5 Microscopic morphology for banana fiber cooked at 90 minutes. A) 0% EDTA under 4x magnified, B) 0% EDTA under 10x magnified, C) 5% EDTA under 4x magnified, D) 5% EDTA under 10x magnified, E) 10% EDTA under 4x magnified, F) 10% EDTA under 10x magnified

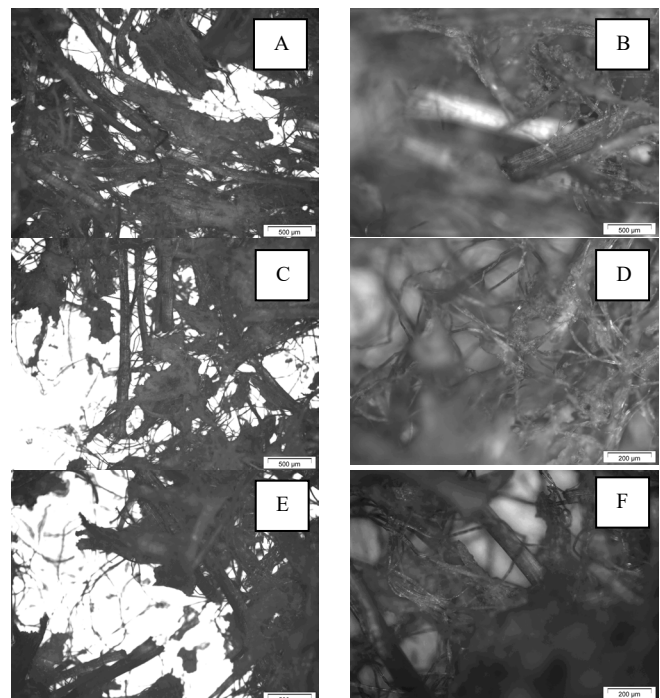


Fig 6 Microscopic morphology for banana fiber cooked at 120 minutes. A) 0% EDTA under 4x magnified, B) 0% EDTA under 10x magnified, C) 5% EDTA under 4x magnified, D) 5% EDTA under 10x magnified, E) 10% EDTA under 4x magnified, F) 10% EDTA under 10x magnified

D. Thermogravimetric analysis

Thermogravimetric analysis (TGA) curve gives an approximation about the weight loss with respect to the temperature due to the release of surface bounded water, volatile matter, hemicellulose, cellulose and lignin present in the sample [9]. TGA curves obtained on the thermogravimetric analysis are shown in Figs 7 and 8. Generally, TGA has three steps where the first step attributes to the degradation of hemicellulose, followed by second and third steps which are cellulose and lignin, respectively [9]. The first steps for TGA curve which the pulp sample treated with EDTA were observed at 36-123°C with only 0.5% of weight loss due to evaporation of water occurs in the fiber and depolymerization of hemicellulose occurs [10].

The major weight loss can be observed in the second step around 200-400°C. In the second step, the weight loss occurs is due to the degradation of cellulose and hemicellulose with the range of weight loss for all the pulp sample is 40-70%. This is due to the longer polymer of glucose units in cellulose molecule and it has higher amount of hydrogen bonds between cellulose chains.

Based on Fig 7, the TGA curve can be conclude as the presence of EDTA can affect the thermal decomposition of pulp. The pulp was cooked for 60 minutes with varying EDTA charge. In addition, when 10% of EDTA was added to the soda pulping process, the curve shift to the right which shows it has high thermal stability. Based on Fig 8, cooking time also can affect the thermal stability. From the TGA curve, 90 minutes of cooking time has the highest thermal stability and 120 minutes has the lowest thermal stability.

Besides, the higher thermal stability of cellulose turns it to possible increasing in thermal decomposition temperature. This can be seen in Table 2 where the thermal decomposition in second steps are higher than the first step. According to Številova et al. [10], decomposition of residual lignin had started at 160°C and slowly decomposed until complete its decomposition by extends its temperature as high as 900°C. Difference on thermal stability for different pulp samples are because of the crystallinity of samples which results from the greater thermal stability of crystalline regions regarding amorphous region [11]. From the table, 60 minutes of cooking time with 10% EDTA shows the highest maximum thermal degradation with 361.59°C and leaving behind a residual weight of 70.1% of the original amount of pulp sample.

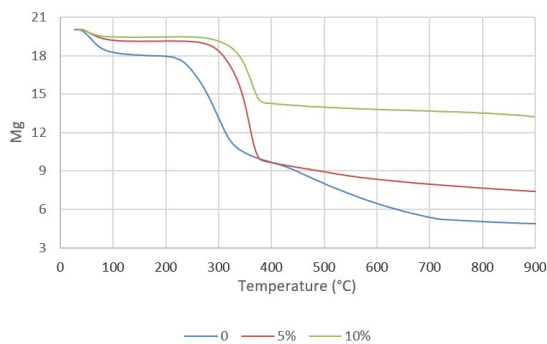


Fig 7 Effect of EDTA charge to the pulp sample

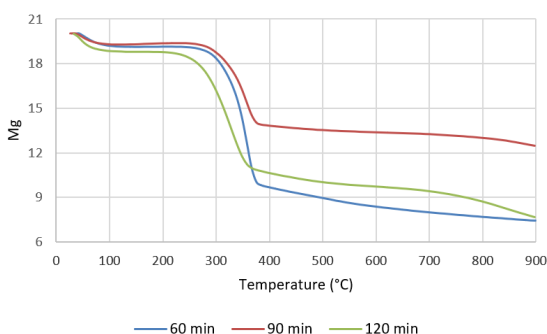


Fig 8 Effect of cooking time to the pulp sample

Table 2: Maximum thermal degradation for soda pulping sample

Sample	Initial Mass Loss (°C)			Maximum TGA (°C)	Residence (%)
	Onset	Max	Endset		
60 min, 0% EDTA	31.89	59	89.96	300	25.8
60 min, 5% EDTA	39.56	56.25	93.98	359.06	43.1
60 min, 10% EDTA	33.44	53.77	78.81	361.59	70.1
90 min, 5% EDTA	31.69	49.06	79.91	358.13	68.4
120 min, 5% EDTA	-	-	-	329.51	50.7

IV. CONCLUSION

Chemical pre-treatment used in this study is found out to be one of the methods that can be introduced for pulping process because it can affect the pulp and paper properties. Besides, addition of EDTA in soda pulping can help to increase the pulp yield. Furthermore, EDTA also can help to protect the cellulose fiber in the pulping process. In the microscopic imaging when EDTA is presence in the pulping process, the fibrous can be clearly seen. As conclusion, banana stem has a potential as raw material for making a paper.

ACKNOWLEDGMENT

Thank you to my supervisor, PM Dr Junaidah Jai and my co-supervisor, Mdm Nurul Amal Nadhirah from the Universiti Teknologi Mara.

References

- [1] K. M. Y. Arafat, J. Nayeem, A. H. Quadery, M. A. Quaiyyum, and M. S. Jahan, "Handmade paper from waste banana fibre," vol. 53, no. 2, pp. 83–88, 2018.
- [2] N. Cordeiro, M. N. Belgacem, I. C. Torres, and J. C. V. P. Moura, "Chemical composition and pulping of banana pseudo-stems," *Ind. Crops Prod.*, vol. 19, no. 2, pp. 147–154, 2004.
- [3] S. Mansouri, R. Khiari, N. Bendouissa, S. Saadallah, F. Mhenni, and E. Mauret, "Chemical composition and pulp characterization of Tunisian vine stems," *Ind. Crops Prod.*, vol. 36, no. 1, pp. 22–27, 2012.
- [4] M. González, L. Cantón, A. Rodríguez, and J. Labidi, "Effect of organosolv and soda pulping processes on the metals content of non-woody pulps," *Bioresour. Technol.*, vol. 99, no. 14, pp. 6621–6625, 2008.
- [5] L. Staffas, E. Pettersson, H. Norrström, T. Ericsson, M. Remberger, and M. Karlsson, *Chelators and eco-labelling of paper products*, no. March. 2017.
- [6] Z. M. A. Ainun et al., "Effect of chemical pretreatment on pulp and paper characteristics of bamboo gigantochloa scorthechinii kraft fibers," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 368, no. 1, pp. 12–18, 2018.
- [7] I. Bicu and F. Mustata, "Optimization of isolation of cellulose from orange peel using sodium hydroxide and chelating agents," *Carbohydr. Polym.*, vol. 98, no. 1, pp.

341–348, 2013.

- [8] A. Alavudeen, N. Rajini, S. Karthikeyan, M. Thiruchitrabalam, and N. Venkateshwaren, “Mechanical properties of banana/kenaf fiber-reinforced hybrid polyester composites: Effect of woven fabric and random orientation,” *Mater. Des.*, vol. 66, no. PA, pp. 246–257, 2015.
- [9] G. C. E, A. E. B, and N. G. I, “Thermo-gravimetry(TGA) and DSC of thermal analysis techniques in production of active carbon from lignocellulosic materials,” *Pelagia Res. Libr. Adv. Appl. Sci. Res.*, vol. 7, no. 2, pp. 109–115, 2016.
- [10] N. Števíulova, V. Hospodárova, and A. Eštoková, “Study of Thermal Analysis of Selected Cellulose Fibres,” *Geosci. Eng.*, vol. 62, no. 3, pp. 18–21, 2016.
- [11] R. Sánchez, E. Espinosa, J. Domínguez-Robles, J. M. Loaiza, and A. Rodríguez, “Isolation and characterization of lignocellulose nanofibers from different wheat straw pulps,” *Int. J. Biol. Macromol.*, vol. 92, pp. 1025–1033, 2016.