

Mechanical and morphological characteristic investigations of deinked used newsprint paper via ultra-sonochemistry method

SAHARMAN GEA^{1*}, SRI RAHAYU¹, ANDRIAYANI¹, AVERROES F PILIANG², NONI OKTARI¹

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Medan 20155, Indonesia.

²Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Medan 20155, Indonesia.

Abstract. Printed newspaper is one of the print-based media published daily in large quantities. The focus of this research is to remove the ink from used newsprint with alkaline treatment by using ultrasound sonochemistry method. Newsprint sheets collected were characterized by mechanical and morphology tests using FT-IR, XRD, tensile test and SEM. FT-IR spectra analysis shows the absorption of C=C functional groups as the main components of newspapers at 1427 and 1635 cm⁻¹ wavelengths. The treatment with alkaline solution increased the mechanical strength properties of paper. SEM morphology analysis result shows that the surface of paper becomes more rough after ultrasound-alkaline treatment compared to paper without ultrasound treatment (conventional treatment). The crystallinity value decreased with alkaline treatment. The longer the ultrasound duration was, the lower the crystallinity degree became.

Keywords: Recycled Newspaper, Deinking, Ultrasound, Alkaline Treatment

INTRODUCTION

Indonesia, as a developing country, has low used paper waste recycling activities. This type of waste mainly comes from used paper where the ink needs to be removed in order to be reused[1]. With the increase of paper production capacity by 5.3% per year[2], Indonesia has the potential to recycle paper waste to reduce the impact of deforestation while meeting the needs of paper [3]. Paper waste mostly comes from daily produced newspapers. Recycled newspapers, however, are not being used back as the base material for printing paper. Until today, they are converted into cardboard papers.

The main constraint of paper recycling is ink removal process. Several processes involve enzymes like laccase [4], cellulase[5] and xylanase[6] obtained from various sources. Although bio-deinking process is categorized as environmentally friendly, the cost required to

prepare enzyme in an industrial scale is high due to the big amount of enzymes needed. Meanwhile, the utilization of chemicals, like magnesium hydroxide, is able to produce pulp with better paper brightness[7]. However, the long-term application in the industrial scale damages the environment.

The application of chemical to remove ink from old newspapers does not allow good quality recycling. Additional practices, such as mechanical methods, need to be done. These methods include vibrations and temperature to break physical interactions among lignin, cellulose and hemicellulose[8], [9]. The effective temperature to obtain paper pulp with high brightness is reported to be between 15°C and 35°C[10], whereas flotation method without involving vibrations and temperature allows the ink to be deposited [11]. The result of deinking from the combination of ultrasound vibration and alkaline in 5–30 minutes time showed slight improvement in the brightness[10]. This result shows that there is an optimum time for deinking process.

Based on the literature study conducted, investigations of time and deinking output need to be carried out by focusing on physical and

*Corresponding Author:
s.gea@usu.ac.id

Received: May 2020 | Revised: June 2020
Accepted: June 2020

morphological characteristics. This study used old newspapers recycled by alkaline method and took longer time to understand the mechanical and morphology properties of the deinking result.

MATERIALS AND METHODOLOGY

Material

Old newspaper samples was supplied by local distributors in Medan, Indonesia. Chemical solutions such as NaOH 2%, $\text{Mg}(\text{OH})_2$ 2%, Na_2SiO_3 2%, H_2O_2 2%, and distilled water were supplied from Sigma-Aldrich.

Preparation of paper pulp

The process to convert sample to pulp followed the previous study done by Singh (2012) [12]. In brief, recycled newspapers were cut into 2-3 cm^2 size and soaked in tap water at room temperature for 24 hours. Then, paper sample was washed for 2-3 times using tap water and crushed by using a mechanical stirrer. Crushed sample was filtered and dried in an oven for 50°C to remove water content. Dried sample was kept in a desiccator.

Ink Removal Process by Conventional Method

Ink removal process from recycled newspapers was done by washing in conventional method. 6 g of dried pulp was soaked in 60 mL aquadest. Then, 6 mL of NaOH 2%, Na_2SiO_3 2% and H_2O_2 2% mixture was mixed into the suspension by using a magnetic stirrer at 70°C for 2 hours. Then the pulp was cooled and washed until neutral pH was reached [13].

Ink removal process by alkaline-based ultrasound method

Ink removal process by ultra-sonochemistry method started by soaking about 6 g of dried pulp into distilled water. The suspension was treated ultrasonically by an ultrasound device (Elmasonik E 15 H) at 37 kHz frequency at 35°C with time variations of 30, 60 and 90 minutes. Then, a mixture of 6 mL of NaOH 2%, Na_2SiO_3 2% and H_2O_2 2% was added into the suspension and stirred at 70°C for 2 hours. The treated pulp was cooled and washed until neutral pH was reached.

The same steps were repeated for deinking process with $\text{Mg}(\text{OH})_2$ substance. In brief, samples with ultrasound treatment at time variations of 30, 60, and 90 minutes were added with 6 mL mixture of $\text{Mg}(\text{OH})_2$ 2%, Na_2SiO_3 2% and H_2O_2 2%. The mixtures were stirred at 70°C for two hours. Then, they were cooled at room temperature and followed by washing process to reach neutral pH.

Afterwards, all of the samples from both NaOH and $\text{Mg}(\text{OH})_2$ treatments were crushed by using a mechanical stirrer. Next, the samples were placed in a paper mold size T150 and dried under the sun to form paper sheets.

Paper Sheet Production

Wet pulps from conventional and ultrasonication ink removal treatments were mashed by using a mechanical stirrer for 5 minutes. Fine pulps were molded and dried. Produced paper sheets were pressed by using an assembly equipment of hot-press with pressure of 50 kg/cm^2 at 105°C temperature for 5 minutes.

RESULTS AND DISCUSSION

Crystal Structure Analysis for Samples with NaOH Treatment

XRD analysis was done to analyze the crystal structure of paper sheet samples. The diffraction patterns of conventional and ultrasonic-NaOH pulp papers are shown in Figure 1 below. Slight differences were observed.

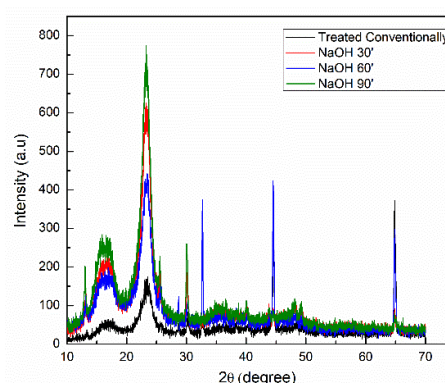


Figure 1. XRD diffractogram of conventional and ultrasound-NaOH papers

Pulp crystallinity values in this study are presented in Table 1. Table 1 shows that alkali solutions affect crystallinity values. This was observed from the variations of crystallinity values in samples with ultrasound-NaOH treatment. From Figure 1, wide diffraction pattern can be observed from conventional pulp paper due to the presence of cellulose, hemicellulose and lignin. Based on its crystallinity and amorphous patterns, crystallographic peak from cellulose was presented in the range of 21.90° and 22.20° , whereas lignin has no crystalline peak [14]. Crystallinity index (CrI) of conventional paper was 86.88% being higher than samples with NaOH-ultrasound treatment for 30, 60 and 90 minutes with values of 74.27%, 74.00% and 73.08% respectively.

Table 1 Crystallinity values of conventional and ultrasound-NaOH papers

Treatment	Time (minute)	Crystallinity (%)
Conventional	-	86.88
Ultrasound-NaOH	30	74.27
	60	74.00
	90	73.08

Crystal Structure Analysis for Samples with $\text{Mg}(\text{OH})_2$ Treatment

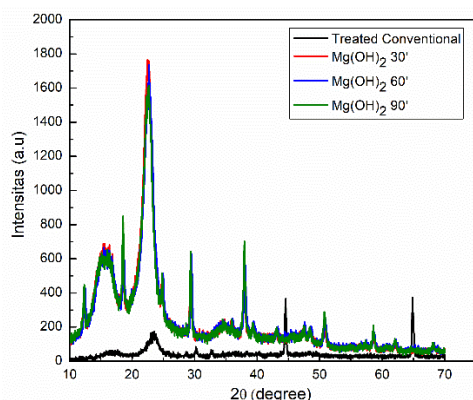


Figure 2. XRD diffractogram of conventional and ultrasound- $\text{Mg}(\text{OH})_2$ treated papers

Figure 2 shows a decrease in crystallinity value in pulp paper samples with $\text{Mg}(\text{OH})_2$ -ultrasound treatment for 30, 60 and 90 minutes in comparison to the sample with conventional treatment. The crystallinity value of pulps in this study is shown in Table 2.

Table 2 Crystallinity values of conventional and ultrasound- $\text{Mg}(\text{OH})_2$ papers

Treatment	Time (minute)	Crystallinity (%)
Conventional	-	86.88
Ultrasound- $\text{Mg}(\text{OH})_2$	30	72.41
	60	71.92
	90	71.49

Table 2 shows that the crystallinity of conventional paper is higher at 86.88% than samples with ultrasound- $\text{Mg}(\text{OH})_2$ treatment at 72.41%, 71.92% and 71.49% crystallinity values. The decrease was caused by alkaline treatment and the duration of ultrasound. This happened because the alkali solution used in the cooking process had selectively attacked lignin (rather than cellulose) which led to degradation

and dissolution. A study reported lignin isolation by using different NaOH concentration left cellulose as the residue from the process [14], [15]. Lignin degradation occurred during the treatment because of the damages in aryl ether chains which comprised 50-70% of total chains in lignin [7].

The data displays amorphous patterns based on the reflection of small angles and 2θ peaks between $25-30^\circ$. There were no changes in the structural patterns of pulp paper. Liquid turbulence and circulation (microstreaming) were produced whenever ultrasonic waves propagated through liquid medium. This has significantly increased mass transfer rate and resulted in the improvement of delignification rate [16].

FTIR Analysis of Samples with NaOH Treatment

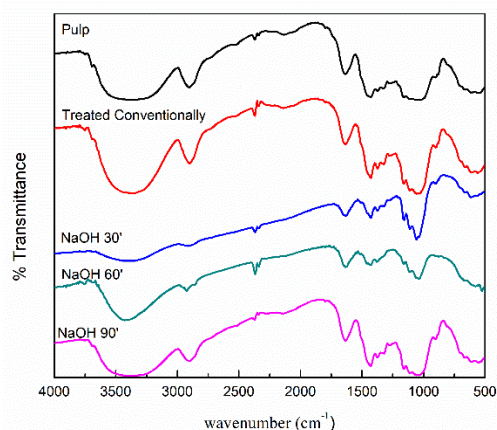


Figure 3. FTIR spectra of samples treated with NaOH

Figure 3 shows FT-IR result of paper pulp, samples with conventional treatment and NaOH-ultrasonication for 30, 60 and 90 minutes. Peaks were observed in FT-IR charts at the transmittance spectra showing the particles interacted with infrared radiation at certain wavelengths. The curves show the bonds of elements in the tested sample. The analysis result can be seen in Table 3.

Figure 3 shows O-H stretching at the peak of 3348 cm^{-1} wavenumber, while wavenumbers $1033-1273\text{ cm}^{-1}$ show the presence of cellulose in the sample. These bands were linked to O-H stretching vibrations and hydrogen bonds among molecules in phenolic and aliphatic structures. The existence of hemicellulose was confirmed in 1273 cm^{-1} and 902 cm^{-1} bands. These bands showed non-conjugated $\text{C}=\text{O}$ stretching in acetyl groups in hemicellulose. The bands in 1427 cm^{-1} and 1635 cm^{-1} showed $\text{C}=\text{C}$ aromatic lignin skeleton. They were the

main components of newspapers. The treatment with ultrasound-NaOH for 60 minutes resulted in higher intensity, 20.809 at wavenumber 2924 cm^{-1} , than the intensity in conventional paper, 11.417 at 2900 cm^{-1} .

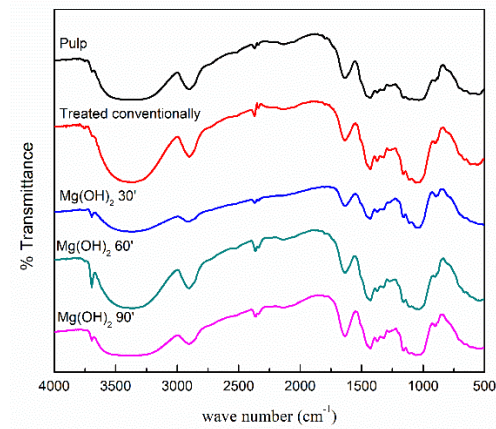


Figure 4. FTIR Spectra of samples treated with $\text{Mg}(\text{OH})_2$

Table 3 Wavenumbers (cm^{-1}) of functional groups in conventional and ultrasound-NaOH papers

Pulp	Convent. treatment	Ultrasound-NaOH			Functional Group
		30 min	60 min	90 min	
3356	3356	3387	3410	3348	O-H
2900	2900	2908	2924	2900	C-H
1635	1635	1635	1635	1635	C=C
1427	1427	1427	1427	1427	O-CH ₃
1273	1273	1280	-	1273	C-O-C
1033	1033	1056	1033	1033	C=O

Table 4 Wavenumbers (cm^{-1}) of functional groups in conventional and ultrasound- $\text{Mg}(\text{OH})_2$ papers

Pulp	Convent. treatment	Ultrasound- $\text{Mg}(\text{OH})_2$			Functional Group
		30 min	60 min	90 min	
3356	3356	3356	3356	3356	O-H
2900	2900	2916	2900	2900	C-H
1635	1635	1635	1635	1635	C=C
1427	1427	1427	1427	1427	O-CH ₃
1273	1273	1280	1273	1280	C-O-C
1033	1033	1033	1033	1033	C=O

FTIR Analysis of Samples with $\text{Mg}(\text{OH})_2$ Treatment

FTIR analysis result of samples with $\text{Mg}(\text{OH})_2$ is shown in Table 4. All samples have got O-H stretching at 3356 cm^{-1} . The analysis result was not far different from the treatment with NaOH-ultrasonication. Based on the functional group

analysis, deinking process by using sonochemistry did not affect the functional groups in the sample. Ultrasonication of $\text{Mg}(\text{OH})_2$ for 30 minutes gave 4.887 intensity at 2916 cm^{-1} wavenumber, which was lower than the intensity of conventional paper sample, 11.417 at 2900 cm^{-1} . The intensity at 3356 cm^{-1} band was strengthened by ultrasonication-alkaline treatment. The ultrasound energy wave moved to break the molecular bonds, causing inked bubbles to be separated from the fibrous parts[17], [18]. This was correlated with the increase of cellulose content in treated newspapers. Hemicellulose bands were still present but lignin had disappeared. This showed that most lignin had been removed with ultrasound-alkaline treatment.

Samples Morphological Characteristics

Morphological analysis of the surface of papers can be seen in Figure 5. The surfaces of paper pulp and conventional paper were smoother. After the alkaline treatment with NaOH and $\text{Mg}(\text{OH})_2$ ultrasound, the surfaces of fibers became rough with the released of some fibers in delignification process. This was in accordance with FTIR results which showed lignin degradation at the surface after alkaline and ultrasound treatments. Other morphological changes, like perforation (small holes in easily torn parts) and cracking, occurred due to hydrolysis by the alkaline. The morphology changes have increased the surface areas of cellulose. When cellulose structure was opened and lignin degradation took place during the procedure, the surface area of cellulose available for alkaline hydrolysis increased[4]. SEM results showed that ultrasonic modified the surfaces of fibers which improved the strength of paper sheets produced.

Mechanical Properties Analysis of Samples with NaOH Treatment

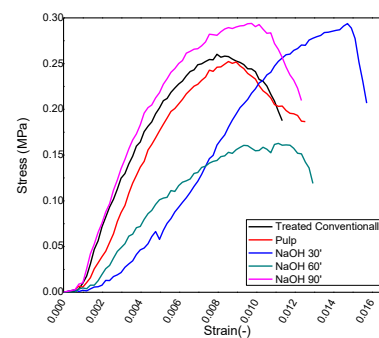


Figure 6 Stress-strain curve of conventional and ultrasound-NaOH papers

Figure 6 shows that all 5 samples gave different curves. In this study, the mechanical properties of papers were tested using tensile strength for samples with ultrasound-NaOH treatment for 30, 60 and 90 minutes. The average thickness of paper produced was 1.0 mm with 80 mm length

and 25 mm width. The tensile strength of each sample is shown in Table 5. The highest Young's Modulus, 58.12736 MPa, was achieved by the sample with 90 minutes NaOH ultrasound.

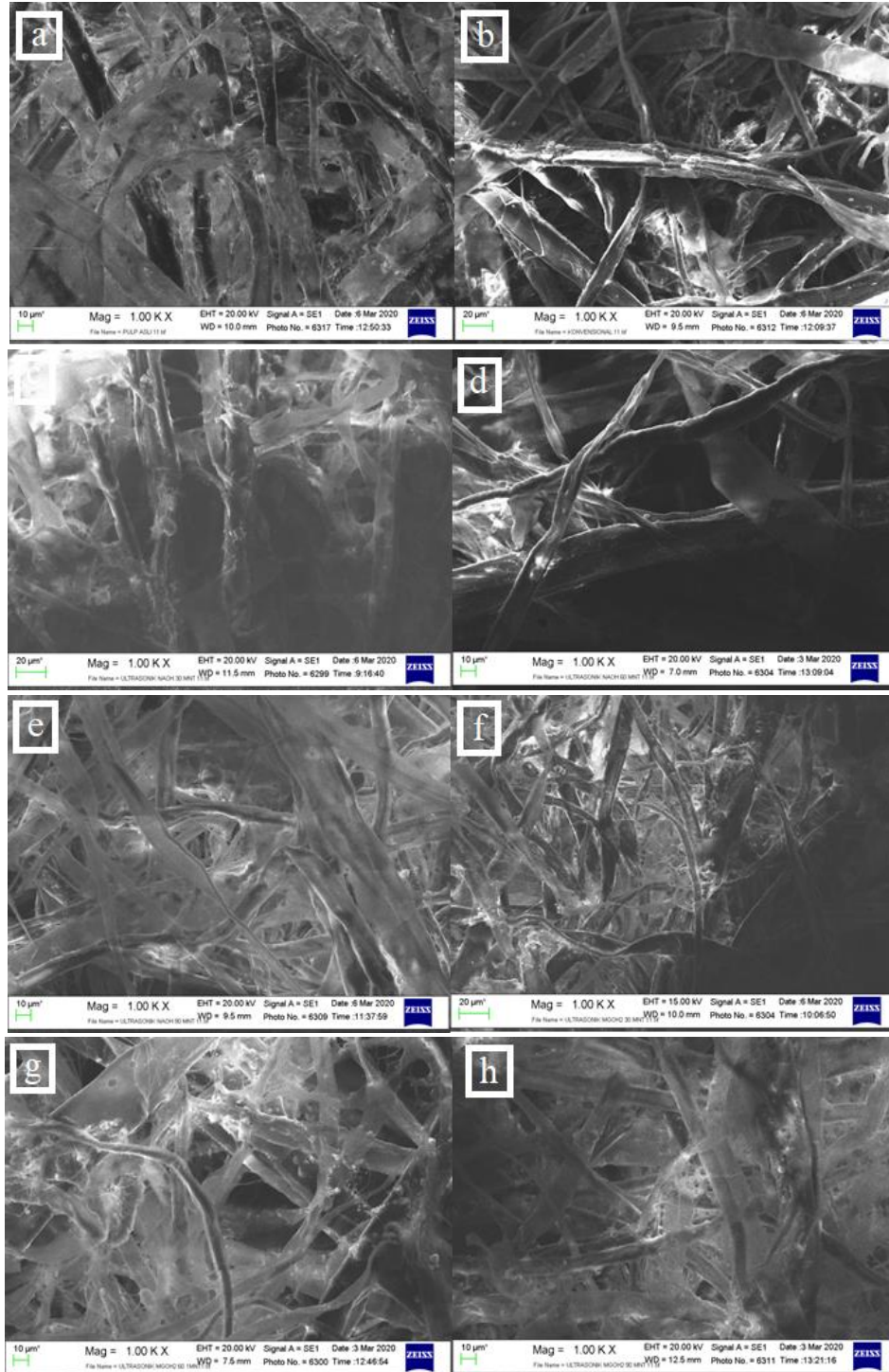


Figure 5 Paper pulp morphology with 1000x magnifications (a) Paper pulp (b) Conventional treatment sample (c) Ultrasound-NaOH 30 min sample (d) Ultrasound-NaOH 60 min sample (e) Ultrasound-NaOH 90 min sample (f) Ultrasound-Mg(OH)₂ 30 min sample (g) Ultrasound-Mg(OH)₂ 60 min sample (h) Ultrasound-Mg(OH)₂ 90 min sample.

Table 5 Mechanical properties of pulp, conventional sample and ultrasound-NaOH sample

Sample	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
Pulp	0.260	1.214	56.059
Conventional treatment	0.260	1.094	56.693
NaOH 30 min	0.260	1.572	31.108
NaOH 60 min	0.260	1.293	38.278
NaOH 90 min	0.260	1.234	58.127

Table 6 Mechanical properties of pulp, conventional sample and ultrasound-Mg(OH)₂ Papers

Sample	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
Pulp	0.260	1.214	56.059
Conventional treatment	0.260	1.094	56.693
NaOH 30 min	0.209	1.453	36.935
NaOH 60 min	0.175	1.134	34.947
NaOH 90 min	0.212	1.373	42.240

Mechanical properties of samples with Mg(OH)₂ treatment

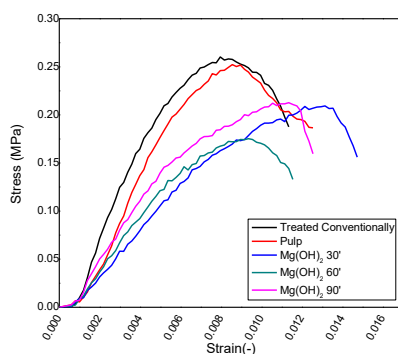


Figure 7 Stress-strain curve of conventional and ultrasound-Mg(OH)₂ papers

The curves in Figure 7 show that the mechanical properties of paper pulp and samples with ultrasonication-Mg(OH)₂ for 30, 60 and 90 minutes have slightly different tensile strength. The highest Young's Modulus, 58.12736 MPa, was achieved by the sample with 90 minutes Mg(OH)₂ ultrasound, while conventional method produced paper has Young's Modulus of 56,69368 MPa. Tensile strength of each paper sample can be seen in Table 6.

The data above can be concluded that NaOH solution was more effective than Mg(OH)₂ in improving mechanic properties of paper. This is because alkali solutions were able to increase carboxyl and carbonyl functional groups content by splitting ester chains in the fibers. Hydrogen bonds with carboxyl and carbonyl groups had higher energy than hydrogen bonds with hydroxyl group only [19]. Hydrogen bonds presented in the paper fibers could increase mechanical properties or tensile strength of the paper produced.

CONCLUSION

The duration of ultrasonication and alkaline solutions used during deinking process of recycled newspapers affect the tensile strength. The highest Young's Modulus, 58.12736 MPa, was obtained at ultrasound-NaOH treatment for 90 minutes, while conventional paper only achieved 56.69368 MPa. The morphological analysis of paper pulp from conventional method showed a smoother surface. Whereas the surfaces after NaOH and Mg(OH)₂ ultrasounds showed rough fiber surfaces. The results aligned with FTIR spectra that showed lignin degradation at the surfaces after alkaline and ultrasonication treatments. There were decreases in crystallinity values in the samples with the addition of alkaline and ultrasonication treatment.

ACKNOWLEDGEMENT

The authors would like to express gratitude to the heads of Cellulose and Functional Material (CFM) Laboratory, Physical Chemistry and Polymer Chemistry Laboratories in the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara for the facility provided during the research.

REFERENCES

- [1] Gil, H. H. A.; Dovale, S. A. M.; VirneyHadely, C. L.; Muñoz, O. A.; Casas, B. A. E.; Quintana, M. G. C.; & Velasquez, J. J. A. 2013. Study of the enzymatic/neutral deinking process of waste photocopy paper. *O Papel*. **74**(8) 61-65.
- [2] Kemenperin: Kapasitas Produksi Kertas dan Bubur Kayu Bakal Naik di 2017. [Online]. Available: <https://kemenperin.go.id/artikel/8421/Kapasitas-Produksi-Kertas-dan-Bubur-Kayu-Bakal-Naik-di-2017>. [Accessed: 08-Apr-2020].

- [3] Gaveau, D. L.; Sheil, D.; Salim, M. A.; Arjasakusuma, S.; Ancrenaz, M.; Pacheco, P.; & Meijaard, E. 2016. Rapid conversions and avoided deforestation: examining four decades of industrial plantation expansion in Borneo. *Sci. Rep.* **6**(1) 1-13.
- [4] Virk, A. P.; Puri, M.; Gupta, V.; Capalash, N.; & Sharma, P. 2013. Combined enzymatic and physical deinking methodology for efficient eco-friendly recycling of old newsprint. *PLoS One*, **8**(8) e72346.
- [5] P. Bajpai. 2014. Deinking with Enzymes, *Recycl. Deinking Recover. Pap.*, no. 2006, pp. 139–153, 2014, doi: 10.1016/b978-0-12-416998-2.00008-8.
- [6] Desai, D. I.; & Iyer, B. D. 2016. Biodeinking of old newspaper pulp using a cellulase-free xylanase preparation of *Aspergillus niger* DX-23. *Biocatal. Agric. Biotechnol.* **5** 78-85.
- [7] Subhedar, P. B.; & Gogate, P. R. 2014. Alkaline and ultrasound assisted alkaline pretreatment for intensification of delignification process from sustainable raw-material. *Ultrason. Sonochem.* **21**(1) 216-225.
- [8] Gea, S.; Panindia, N.; Piliang, A. F.; Sembiring, A.; & Hutapea, Y. A. 2018. All-cellulose composite isolated from oil palm empty fruit bunch. *Journal of Physics: Conference Series* **1116** (4) 042013 doi: 10.1088/1742-6596/1116/4/042013.
- [9] Gea, S.; Zulfahmi, Z.; Yunus, D.; Andriyani, A.; & Hutapea, Y. A. 2018. The isolation of nanofibre cellulose from oil palm empty fruit bunch via steam explosion and hydrolysis with HCl 10%. *Journal of Physics: Conference Series* **979**(1) 012063. doi: 10.1088/1742-6596/979/1/012063.
- [10] Gaquere-Parker, A. C.; Ahmed, A.; Isola, T.; Marong, B.; Shacklady, C.; & Tchoua, P. 2009. Temperature effect on an ultrasound-assisted paper de-inking process. *Ultrason. Sonochem.* **16**(5) 698-703.
- [11] Lane, G., Macías, M., & Miller, N. 2010. Influence of paper and ink on deinking of inkjet prints. *2010 TAPPI PEERS Conf. 9th Res. Forum Recycl.* **2** 1736–1756.
- [12] Singh, A.; Yadav, R. D.; Kaur, A.; & Mahajan, R. 2012. An ecofriendly cost effective enzymatic methodology for deinking of school waste paper. *Bioresour. Technol.* **120** 322-327.
- [13] Xu, Q. H.; Wang, Y. P.; Qin, M. H.; Fu, Y. J.; Li, Z. Q.; Zhang, F. S.; & Li, J. H. 2011. Fiber surface characterization of old newsprint pulp deinked by combining hemicellulase with laccase-mediator system. *Bioresour. Technol.* **102**(11) 6536–6540.
- [14] Gea, S.; Siregar, A. H.; Zaidar, E.; Harahap, M.; Indrawan, D. P.; & Perangin-Angin, Y. A. 2020. Isolation and characterisation of cellulose nanofibre and lignin from oil palm empty fruit bunches. *Materials* **13**(10) 2290.
- [15] Gea, S.; Panindia, N.; Piliang, A. F.; Sembiring, A.; & Hutapea, Y. A. 2018. All-cellulose composite isolated from oil palm empty fruit bunch. *Journal of Physics: Conference Series* **1116**(4) 042013. doi: 10.1088/1742-6596/1116/4/042013.
- [16] Wu, J.; Lin, L.; & Chau, F. T. 2001. Ultrasound-assisted extraction of ginseng saponins from ginseng roots and cultured ginseng cells. *Ultrason. Sonochem.* **8**(4) 347-352.
- [17] Zainul, R.; Alif, A.; Aziz, H.; Arief, S.; Syukri, and Yasthopi, A. Photoelectrosplitting water for hydrogen production using illumination of indoor lights. *J. Chem. Pharm. Res.*, **7**(11) 57-67.
- [18] Candani, D.; Ulfah, M.; Noviana, W.; & Zainul, R. 2018. Review pemanfaatan teknologi sonikasi. Universitas Negeri Padang.
- [19] Wistara, N.; and Young, R.A. 2000. Properties and treatments of pulps from recycled paper . Part I . Physical and chemical properties of pulps,” *Cellulose* **6**(4) 291–324.