ALKIMIA : Jurnal Ilmu Kimia dan Terapan

ARTICLES

View Article Online
View Journal | View Issue

OPEN ACCESS

Magnetic-Hydrochar from Galam Bark Waste (*Malaleuca cajuputi*) as Sasirangan Waste Adsorbent

Hanna Habibah[a], Risaldi Ridwan[a], Desmalina Safitri[a], Sunardi[a]*

Abstract. Galam wood (*Malaleuca cajuputi*) is one of the woody plants that is able to grow well in the peat swamp environment of the South Kalimantan wetlands. Research on the synthesis and characterization of magnetic-hydrochar from galam bark waste for the treatment of sasirangan liquid waste has been carried out. This study aims to determine the characteristics of hydrochar and magnetic-hydrochar against the adsorption ability of sasirangan liquid waste. The results showed that the modification of galam bark into hydrochar and magnetic-hydrochar produced different characteristics based on the analysis of functional groups of infrared spectra. The surface morphology of hydrochar and magnetic-hydrochar also showed the significant differences based on scanning electron microscope (SEM) analysis. The resulting magnetic-hydrochar showed a higher adsorption ability to sasirangan waste than the hydrochar of galam bark and galam bark without modification.

Keywords : Adsorbtion, galam waste, magnetic-hydrochar, sasirangan

[a]*Lambung Mangkurat University, Banjarbaru, Indonesia*
Correspondence and requests for materials should be addressed to Sunardi, S.
(email: sunardi@ulm.ac.id)

Introduction

Sasirangan is a typical fabric from southern Kalimantan that has many motifs. It is noted that there are a total of 35 Sasirangan Batik Home Industries in Banjarmasin City that have started production and distribution activities since 1986 until now. The production of sasirangan fabric is famous for the manufacturing process, namely by dismoke or dijelujur then given various kinds of dyes. Dyes that are widely used are synthetic dyes such as indhanthrene, naphthol and frosion. Based on the results of research on sasirangan home industry with samples in areas affected by pollution of the Martapura river as a central river in South Kalimantan, there is one sample that has a value above the quality standard of 107.93 TCU [1].

The discharge of textile industry wastewater into the environment without a treatment process can damage the ecosystem and become toxic to aquatic organisms, even some types of dyes are suspected to be carcinogens and endanger human health [2]. Some methods to reduce the color concentration in wastewater include: filtration, coagulation, precipitation, reverse osmosis, oxidation, reduction, solvent extraction, and membrane separation. These methods have disadvantages because they require high operational costs, long processing times and produce secondary pollutants [3].

Alternative methods that are currently widely studied because of their superior selectivity, economical, environmentally friendly and operationally efficient are adsorption. Absorption is the process of mass transfer on the surface of pores in granules of adsorbent, a solid material with a very large inner surface area. The material which is an adsorbent has very porous properties that support the absorption process, especially on the pore walls. The use of adsorbent materials from hydrochar or biochar resulting from hydrothermal carbonization (HTC) has the potential to be developed because lignocellulose, pore-forming components and active groups that are constituents of hydrochar can be obtained from the abundance of biomass.

Biomass that contains a lot of lignocellulose and has the potential to be used as hydrochar is Galam (*Melaleuca cajuputi*). Galam is a native swamp wood plant that grows in shallow peat forests and dominates swamp forests in South Kalimantan. The content of galam wood consists of hemicellulose 27.42%, lignin 18.28%, cellulose 47%, water content 1.86%, ash content 1.33% and impurities 4.11% where the lignocellulose content studied is relatively high. In addition, galam is a type of fast-growing tree so that many are produced by the people of South Kalimantan with total production in Barito Kuala Regency reaching 20,000 cubic meters per year. The production of galam wood produces waste in the form of residual pieces of wood chips and becomes organic waste because it is disposed of around the production site without processing [4].

The purpose of this study is to utilize galam bark waste as an adsorbent for sasirangan liquid waste and its problems in the environment and optimize the potential of galam wood as a typical plant of South Kalimantan. Galam bark waste is converted into pure hydrochar (pristine hydrochar) and magnetic hydrochar to improve the adsorption ability against sasirangan liquid waste.

Experimental

Materials

Materials that used are blenders, stirring rods, petri dishes, erlenmeyer, beaker cups, measuring cups, filter paper, plastic funnels, ovens (Local), analytical balance sheets (Ohaus), tweezers, sieves, universal indicators, sudip, orbital shakers, magnetic stirrers KJ-201BD, vial bottles, magnets, label paper, galam bark waste, sasirangan waste, aquifers, NaOH, $Fe_2SO_4.7H_2O$, and $FeCl_3$.

Hydrochar Synthesis

Galam bark is collected and dried in the sun then the material is mashed using a 60 mesh sieve to obtain a smaller particle size and the same size. Then it is introduced into a 2% NaOH solution and stirred in a stirrer at a temperature of 80 °C for 60 minutes. The mixture is then filtered with filter paper and evaporated using an oven at a temperature of 100 °C for 1 hour then allowed to stand. Samples that have been pretreatmented were weighed as much as 8 grams. The sample was then put into a hydrothermal reactor and 80 mL of aqueous was added and stirred until all samples were submerged. After all samples are submerged the hydrothermal reactor is then closed and put in an oven with a temperature of 200 °C for 6 hours. The sample that has been hydrothermalized is then cooled and filtered using filter paper and then evaporated at a temperature of 60 °C for 24 hours. The evaporated sample is then weighed to determine the change in mass.

Magnetic Hydrochar Synthesis

Weighed $FeCl_3$ as much as 3 grams and $Fe_2SO_4.7H_2O$ as much as 6 grams and then put into 300 ml of aqueous. The solution is stirred to a homogeneous state. The homogeneous solution is then added with a hydrochar sample of 9 grams and stirred. The solution that has been mixed with the hydrochar sample is then personified for 10 minutes at a room temperature of 30 °C. After personification is measured and set the pH of the solution to 11 by adding a naoh solution little by little. The solution formed with a pH of 11 is then stirred at room temperature using a stirrer for 25 minutes. The solution is then allowed to stand for overnight and then filtered using filter paper. The obtained residue is then rinsed with aqueous.

Characterization

Physical and chemical properties of hydrochar and magnetic hydrochar were characterized by FTIR, SEM-EDX, and UV-Vis Spectrophotometers. Fourier transform infra-red (FTIR) analysis was used to verify the presence of surface functional groups in hydrochar samples [5]. Scanning electron microscope (SEM) analysis is used to determine the surface morphology of magnetic hydrochar. Meanwhile, UV-Vis spectrophotometric analysis is used for the absorbance value of sasirangan wastewater and wastewater that has been treated with magnetic hydrochar.

Magnetic hydrochar Adsoption Capacity

Magnetic hydrochar is weighed as much as 0.5 grams and put in an erlenmeyer. Then 50 mL of sasirangan liquid waste was added to the erlenmeyer. Next the mixture is stirred with an orbital shaker for 60 minutes at a speed of 120 rpm at room temperature. The solution is filtered and the filtrate is taken to measure its absorbance using a UV-Vis Spectrophotometer. All absorption experiments were carried out three times.

The adsorption ability (%) of the adsorbent for adsorption against sasirangan liquid waste can be calculated by the following equation:

$$\%\ Adsorption = \frac{A_{0-A_i}}{A_o}\ x\ 100\%$$

Where %Adsorption is the adsorption ability (%), Ao is the initial absorbance value and Ai is the absorbance value after adsorption.

Results and Discussion

Hydrochar Synthesis

In this study, hydrochar was synthesized from galam bark bomassa obtained from Liang Anggang District, Banjarbaru. The collected galam bark is further dried in the sun. The drying process with sunlight aims to remove the moisture content contained in the galam bark. The dried galam bark is further smoothed and sifted using a 60 mesh sieve. The purpose of smoothing is to obtain galam bark of smaller size. Sifting is carried out with the aim of obtaining galam bark of uniform size. In addition, galam bark that has a smaller size aims to make the hydrothermal carbonization process can produce optimal hydrochar because the heat generated in the carbonization process will be evenly distributed throughout the biomass included in the autoclave reactor.

The dry and uniform galam bark was then carbonized using the hirotermal method with a temperature of 200oC within 6 hours. The function of combustion with this hydrothermal method is to increase the carbon content in biomass and convert biomass into hydrochar [6]. The hydrochar obtained from the hydrothermal carbonization process is then filtered and dried for 24 hours using an oven at a temperature of 60 °C. the filtration aims to separate between filtrate (water) and residue (hydrochar). Drying hydrochar for 24 hours aims to obtain hydrochar that is free of water. Images of galam bark powder and hydrochar synthesis results can be seen in figure 1.

Magnetic hydrochar synthesis

Figure 1. Powder (a) galam (b) hydrochar from galam bark waste

Magnetic hydrochar synthesized with $Fe_2SO_4.7H_2O$ and $FeCl_3$. The ingredients $Fe_2SO_4.7H_2O$ and $FeCl_3$ are mixed into the aqueous and stirred until homogeneous. The stirring function is so that the mixture quickly dissolves in aqueducts and forms a solution. Magnetic hydrochar was successfully synthesized from hydrochar, this is evidenced by the interest of hydrochar by magnets during the experiment. It has been reported that hydrochar surfaces help the neclueation of iron precipitation oxides in alkaline media, through close chemical bonds between oxygenated groups (hydroxyl and carboxyl) presented in hydrochar and iron hydroxide/oxide in solution, producing minerals to hydrochar. The picture of the synthesis of magnetic hydrochar can be seen in figure 2.

Characterization

Fourier Transform Infra-Red (FTIR)

Magnetic hydrochar synthesis results were further analyzed using fourier tarnsform infra-red (FTIR). This FTIR analysis aims to determine the presence of functional groups in hydrochar and magnetic hydrochar. The results of FTIR spectra from galam, hydrochar and magnetic hydrochar can be seen in figure 3.

Based on the characterization results, it shows that the spectrum of galam, hydrochar and magnetic hydrochar contains the -OH stretching, C-O, C=C, C=O, and C-H functional groups. The difference between galam, hydrochar and magnetic hydrochar lies in the galam without modification there is an absorption band of 856 cm^{-1}, namely the strain of the β-glycosidic bond in cellulose while in hydrochar and magnetic hydrochar there is no. There is still a strain of β-glycosidic

Figure 2. Magnetic hydrochar from galam bark waste

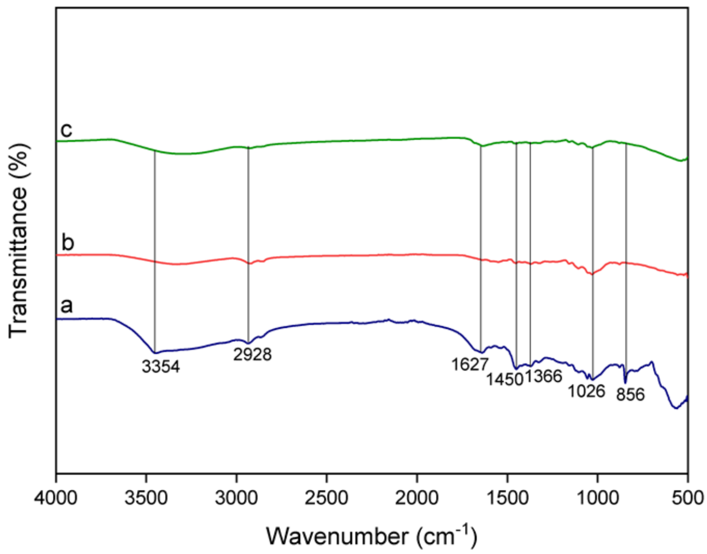

Figure 3. Spectrum FTIR (a) galam (b) *hydrochar* (c) *magnetic hydrochar*

bonds in the galam caused by the galam not being heated or without treatment so that the glycosidic bonds are still present in the cellulose biomass of galam wood. The groups that can be found in magnetic hydrochar there is a carbonyl group, hydroxyl where the functional group can function as an active functional group for the absorption process [7]. Based on the results of the FTIR spectra in figure 3 shows that in the galam, hydrochar and magnetic hydrochar contain functional groups that can be seen in table 1.

Scanning Electron Microscope (SEM)

Hydrochar and magnetic hydrochar synthesis results are further characterized using a sacnning electron microscope (SEM). This SEM analysis aims to determine the surface morphology of hydrochar. The results of sem analysis on galam, hydrochar and magnetic hydrochar can be seen in figure 4.

Based on SEM galam images, hydrochar and magnetic hydrochar at an enlargement of 5000x show the surface morphology of galam which is still regular, still visible fiber form from cellulose. In hydrochar and magnetic hydrochar, there are changes in substrate morphology that are observed, namely damage in the biomass structure with hydrothermal treatment, while in magnetic hydrochar. coarser and porous surface. This shows the decomposition of the hemicellulose component in biomass after being converted from galam to magnetic hydrochar through a hydrothermal process. Based on Wang's report, et al. [8] states that polymers such as hemicellulose can easily decompose into fragments, causing a rougher morphology of the resulting residue surface.

Adsorption Capacity

This study was conducted to determine the effect of hydrochar modified into magnetic hydrochar on the absorption capacity of sasirangan waste. In the absorption capacity test, it was carried out using a magnetic hydrochar mass of 0.5 grams, the stirring time was 60 minutes with a stirring speed of 120 rpm. Pictures of sasirangan liquid waste and the results of the sasirangan liquid waste adsorption test with

Tabel 1. Perbandingan hasil analisis FTIR *hydrochar* dan *magnetic hydrochar*

Wavenumber	Functional Clusters	Wavenumber (cm^{-1})			Refference
		a	b	c	
860 cm^{-1}	Strain of β-glycosidic bonds in cellulose	856			Wilk, *et. al.*, 2020 [9]
1030 cm^{-1}	C-O strain on cellulose	1026	1032	1032	Kang, *et. al.*, 2018 [10]
1378 cm^{-1}	Deformation of C-H bonds in cellulose and hemicellulose	1366		1373	Sevilla, *et. al.*, 2011 [6]
1457 cm^{-1}	C=C strain on lignin	1450	1450		Wilk, *et. al.*, 2020 [9]
1638 cm^{-1}	C=O strain on lignin	1627		1637	Cheng, *et. al.*, 2019 [11]
2927 cm^{-1}	–CH strain of the methyl and methylene groups in lignin and cellulose	2923	2929	2923	Pinheiro & Barros, 2020 [12]
3350 cm^{-1}	Strain –OH	3390	3354	3354	Zhu, *et. al.*, 2017 [13]

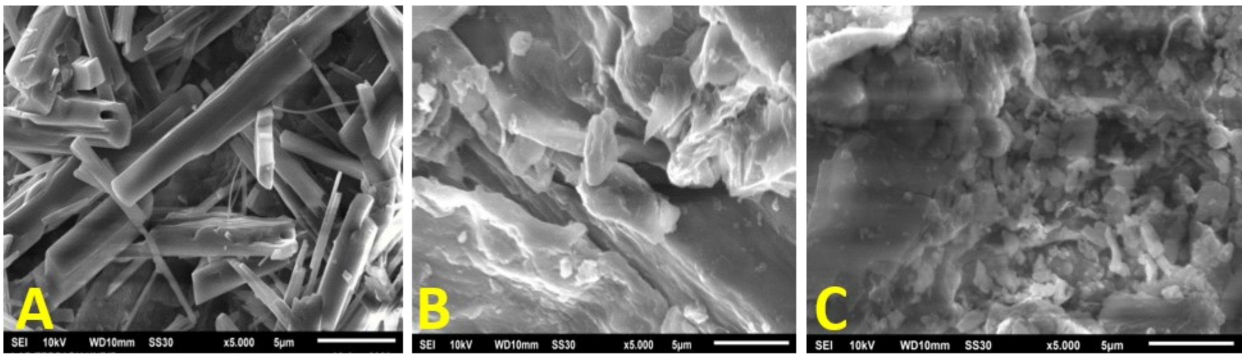

Figure 4. SEM (a) galam (b) *hydrochar* (c) *magnetic hydrochar*

galam adsorbent, hydrochar and magnetic hydrochar can be seen in figure 5.

The results of the absorption qualitative test on liquid waste sasirangan for adsorbent galam waste still look colored which indicates that galam without modification is not good at absorbing dyestuffs in waste. In hydrochar waste looks more clear yellowish. The color of the waste that was originally dark blue becomes clearer after being processed with hydrochar which indicates that the hydrochar has a good absorption ability against sasirangan liquid waste. Meanwhile, the results of the absorption test using magnetic hydrochar wastewater which was originally colored after processing appeared visually clear. So it can be said that magnetic hydrochar is modified from galam to hydrochar which is then further modified so that it becomes magnetic hydrochar has a good absorption ability at a stirring time of 60 minutes. Based on the data from the adsorption capacity test obtained, it can be seen in figure 6.

Figure 6 shows that the type of adsorbent and the length of time of stirring can affect the absorption capacity value. Based on the data obtained, sasirangan waste has a maximum wavelength of 603 nm with an absorption of 0.367. The best absorption capacity value on the hydrochar is shown at the stirring time for 60 minutes with an absorption capacity of 81.5%, while the best absorption capacity for magnetic hydrochar is shown at a stirring time of 60 minutes with an absorption capacity of 94.3%. Galam converted into hydrochar will increase the absorption capacity of galam as an adsorbent. This can be seen in table 2 where the galam which has an absorption capacity of 24.3% can increase to 81.5 after the galam is modified into hydrochar. Hydrochar that has a better abspirance capacity than galam can be increased absorption ability by making modifications to the hydrochar. The modification of hydro-

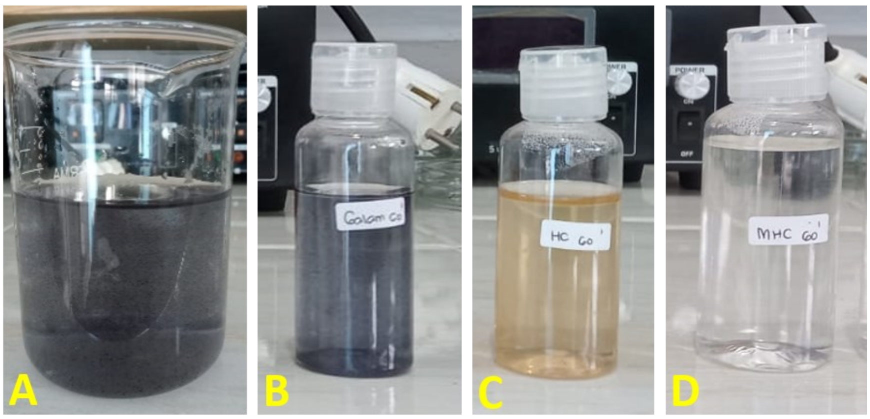

Figure 5. Absorption test of sasirangan waste with (a) sasirangan waste (b) galam (c) hydrochar (d) magnetic hydrochar

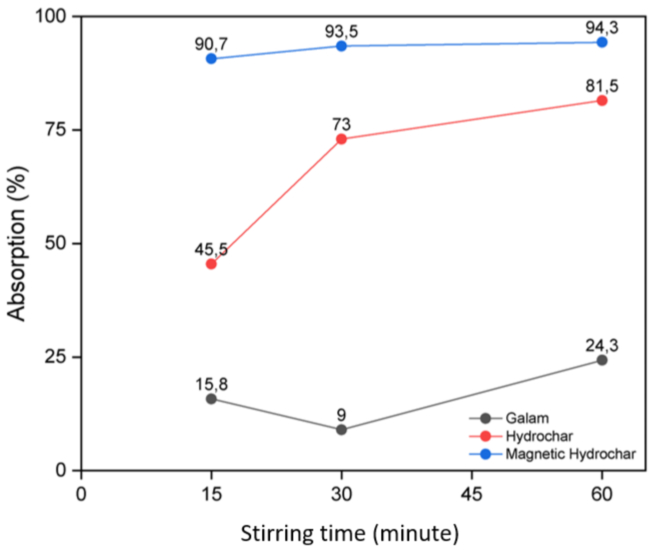

Figure 6. Effect of stirring time and type of adsorbent on color removal

char to magnetic hydrochar increases the absorption ability of liquid waste compared to hydrochar without modification. The absorption ability of hydrochar by 81.5% can be increased to 94.3% by modifying it to magnetic hydrochar.

In addition, based on the results of the absorption capacity test, it shows that magnetic hydrochar has the greatest ability to absorb dyestuffs compared to hydrochar and galam. This is shown based on the value of the absorption capacity of magnetic hydrochar which has a greater efficiency compared to the value of hydrochar absorption capacity and also galam for the same time and stirring speed. Thus hydrochar modified into magnetic hydrochar can increase the ability of the hydrochar in absorbing dyestuffs or heavy metals.

Conclusion

Magnetic hydrochar synthesis has the characteristic of containing hydroxyl and carbonyl functional groups that are good for absorption. The surface morphology in magnetic hydrochar is rougher and irregular compared to hydrochar. Modification of hydrochar to magnetic hydrochar can significantly increase the absorption capacity of sasirangan liquid waste.

Acknowledgements

The Author would like to thank the Ministry of Education, Culture, Research, and Technology for funding this research through the PKM-RE program in 2022.

References

[1] Nasruddin, N., Nurandini, D., Halang, B., Kumalawati, R., Syaharuddin, S., Riadi, S., & Farista Aristin, N. 2018. Identifikasi Potensi Limbah Cair Zat Pewarna Sasirangan terhadap Pencemaran di Kota Banjarmasin. [online]: https://repo-dosen.ulm.ac.id//handle/123456789/16553

[2] Khair, R. M., Prihatini, N. S., Apriani, & Primaningsih, V. 2021. Penurunan Konsentrasi Warna Limbah Cair Sasirangan Menggunakan Absorpsi Limbah Padat Lumpur-Aktif Teraktivasi Industri Karet. Jurnal Teknik Lingkungan. 7(1): 74-83. doi: 10.20527/jukung.v7i1.10822

[3] He, X., Zhang, T., Xue, Q., Zhou, Y., Wang, H., Bolan, N. S., & Tsang, D. C. 2021. Enhanced adsorption of Cu (II) and Zn (II) from aqueous solution by polyethyleneimine modified straw hydrochar. Science of the Total Environment. 778: 146116. doi: 10.1016/j.scitotenv.2021.146116

[4] Anggarini, E., & Muzaidi, I. 2021. Pemanfaatan Limbah Kayu Galam Barito Kuala sebagai Pengganti Agregat Kasar pada Campuran Beton. Konstruksia. 12(1): 61-68. doi: 10.24853/jk.12.1.61-68

[5] Xue, Y., et al. 2012. Hydrogen Peroxide Modification Enhances The Ability of Biochar (Hydrochar) Produced from Hydrothermal Carbonization of Peanut Hull to Remove Aqueous Heavy Metals: Batch and Column Tests. Chemical Engineering Journal. 673-680. doi: 10.1016/j.cej.2012.06.116

[6] Sevilla, M. & Fuertes, A. B. 2009. The Production of Carbon Materials by Hydrothermal Carbonization of Cellulose. Carbon. 47 (9): 2281-2289. doi: 10.1016/j.carbon.2009.04.026

[7] Kruer-Zerhusen, N., Cantero-Tubilla, B., and Wilson, D.B. 2018. Characterization of Cellulose Crystallinity After Enzymatic Treatment Using Fourier Transform Infrared Spectroscopy (FTIR). Cellulose. 25(1): 37-48. doi: 10.1007/s10570-017-1542-0

[8] Wang, T., Zhai, Y., Zhu, Y., Li, C. dan Zeng, G. 2018. A Riview of The Hydrothermal Carbonization of Biomass Waste for Hydrochar Formation: Process Conditions, Fundamentals, and Pshycochemical Properties. Renewable and Suistanable Energy Riviews. 90: 223-247. doi: 10.1016/j.rser.2018.03.071

[9] Wilk, M., Magdziarz, A., Kalemba-Rec, I., dan Szymanska-Chargot, M. 2020. Upgrading of Green Waste into Carbon-rich Solid Biofuel by Hydrothermal Carbonization: The Effect of Process Parameters on Hydrochar Derived From Acacia. Energy. 202(1): 1-13. doi: 10.1016/j.energy.2020.117717

[10] Kang, C., Zhu, L., Wang, Y., Xiao, K. dan Tian, T. 2018. Adsorption of Basic Dyes Using Walnut Shell-based Biochar Produced by Hydrothermal Carbonization. Chemichal Research in Chinese Universities. 34(4): 622 -627. doi: 10.1007/S40242-018-8018-0

[11] Cheng, J., Yue, L., Ding, L., Li, Y. Y., Ye, Q.,

Zhou, J., Cen, K. dan Lin, R. 2019. Improving Fermentative Hydrogen and Methane Production form an Algal Bloom Through Hydrothermal/Steam Acid Pretreatment. International Journal of Hydrogen Energy. 44 (12):5812-5820. doi: 10.1016/j.ijhydene.2019.01.046

[12] Pinheiro, N. P. F. dan Barros, N. E. L. 2020. Steam Exploxion: Hydrothermal Pretreatment in The Production of an Adsorbent Material Using Coconut Husk. Bioenergy Research. 1-10. doi: 10.1007/s12155-020-10159-y

[13] Zhu, G., Xing, X., Wang, J. dan Zhang, X. 2017. Effect of Acid and Hydrothermal Treatments on The Dye Adsorption Properties of Biomass-Derived Activated Carbon. Journal of Material Science. 52(13): 7664-7676. doi: 10.1007/s10853-017-1055-0