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Synthesis of Graphene Oxide from Sugarcane Bagasse by Using Modified Hummers Method as a Microwave Absorber

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ABSTRACT

One of the industrial wastes that was difficult to decompose was bagasse. Bagasse was the residue from sugarcane processing, chosen as a raw material because it has the potential as a carbon source that was eco-friendly, inexpensive, and easy to find. The aim of this research is the synthesis of graphene oxide derived from bagasse. The method used in this study was the modified Hummers method, which is a modified method of the original Hummers method with the addition of thermal treatment at the initial stage of synthesis to increase the efficiency and quality of synthesis. Furthermore, this modification can also reduce synthesis time and minimize the risk of damage to the raw material. After the synthesis process was completed, the produced graphene oxide was characterized using various analytical techniques, including Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The synthesized graphene oxide was then tested for its ability to absorb microwaves at X-band frequencies (8-12 GHz). The characterization results indicate that the synthesized graphene oxide possesses a homogeneous structure with thin graphene layers and a clean surface. Moreover, the graphene oxide also exhibits excellent microwave absorption properties at an X-band frequency of 10.16 GHz, with a reflection loss value of -23.94 dB, absorption coefficient of 93.65%, and absorption bandwidth of 1.13 GHz. The test results demonstrate that the graphene oxide derived from bagasse exhibits significant absorption capabilities towards microwaves at specific frequencies. This indicates the potential application of graphene oxide as an effective microwave absorber material.

Keywords : *bagasse; graphene oxide; modified Hummers method; microwave absorber.*

I. INTRODUCTION

Bagasse is a waste that has fibers that take a long time to decompose. Bagasse can be decomposed by burning, but the process of burning bagasse can cause pollution, so another method is needed to reduce bagasse waste. The high carbon content in bagasse is the basis for using it as activated carbon [1]. Bagasse contains lignocellulose (cellulose, hemicellulose, and lignin) which forms complex chemical bonds [2]. It is estimated that the polysaccharide content in sugar cane reaches 70%, consisting of 50% - 55% cellulose and 15% - 20% hemicellulose, lignin is estimated to only be around 20% - 23%, and the rest is in the form of ash compounds. This is the reason why bagasse can be used as a material for making graphene oxide.

Graphene oxide (GO) is a sheet of graphite oxide obtained by exfoliating graphite oxide into a layered sheet that contains only one or a few layers of carbon atoms through sonication or mechanical stirring [3]. GO can be reduced partially to graphene-like sheets by removing oxygen-containing groups through the restoration of the conjugated structure referred to as reduced GO (rGO). These rGO sheets are usually considered to be one type of chemically derived graphene that has similar properties to pure graphene. Graphene and GO are very different, where graphene consists only of sp^2 hybridized carbon atoms, while GO has a carbon structure that is decorated

by various oxygen functional groups. GO can be used for various things, such as seawater desalination, batteries, anti-bacterial plasters, wall paints, field effect transistors (FET), and in the biomedical field [4].

GO can be produced using inexpensive graphite by applying cost-effective chemical methods with simple processes and high yields. Furthermore, GO is highly hydrophilic and can form stable aqueous colloids to facilitate the assembly of macroscopic structures by a simple and low-cost solution process [5]. The conventional way to convert graphite oxide into GO is carried out by mechanically exfoliating the graphite oxide, by sonication of graphite oxide in water or a polar organic medium into completely exfoliated GO flakes [6]. In addition, through mechanical stirring of graphite oxide in water, graphite oxide can also be well exfoliated into GO [7]. The sonication and mechanical stirring methods can be combined together to exfoliate the graphite oxide producing a better efficiency than the individual methods separately.

Natural graphite and synthetic graphite have several constraints as the precursors in the production of GO, where the natural sources of graphite are limited in some countries and the production process of synthetic graphite requires extremely high temperatures (≥2500°C) and demands utmostly high cost [8]. Meanwhile, biomass waste has been widely recommended as a potential precursor material for carbon-based synthesis due to its environmental-friendly characteristic, lower temperature process, abundant availability, geographically wide spreading, and lower cost requirements compared to conventional graphite. Several recent studies have suggested biomass as a very appropriate alternative starting material for preparing valuable carbonaceous materials. In the United States, more than 7 billion gallons bioalcohol were produced in 2007. In Brazil, almost all the light automobiles are running on the blend of gasoline and bioalcohol, and similar scales can be easily envisaged for materials, appropriate carbon products assumed. Even more abundant, waste biomass derived from agricultural resides and forest byproducts has drawn little attention as a raw material, since only simple combustion has been used to elevate the value of waste biomass [9]–[11]

The high carbon content in sugarcane bagasse serves as the basis for utilizing it as activated carbon. Graphene oxide derived from activated carbon-based sugarcane bagasse can enhance the absorption of microwaves by a material [12]. In simple terms, graphite is oxidized to form graphite oxide (GO), and then the layers of graphite oxide are exfoliated in water to form graphene oxide [13].

The other form of application of graphene oxide is in the form of microwave absorption. Microwaves are a form of electromagnetic energy that is converted into heat through interactions between the electric wave-generating components and charged particles of the material used. Generally, microwave radiation is associated with various electromagnetic radiations with frequencies ranging from 300 MHz to 300 GHz. Domestic and industrial microwave applications typically operate at a frequency of 2.45 GHz, which corresponds to a wavelength of 12.2 cm and an energy of 1.02×10^{-5} eV [14]. Along with the development of technology, microwaves are an important component because they can be used in the field of communication such as in radar technology, analyzing atomic and molecular structures, guiding aircraft landing, and detecting the presence of an object. Graphene oxide based on sugarcane bagasse activated carbon can increase the absorption of microwaves of a material. Based on the benefits of graphene oxide and the availability of bagasse as a carbon source that is cheap and easy to find, this research aims to utilize bagasse as an ingredient in the synthesis of graphene oxide.

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II. METHOD

This type of research was experimental research. This research examines the analysis of the properties of microwave absorbers made from sugarcane bagasse waste using the modified Hummers method. The Hummers method was a graphene synthesis method that is better than the previous method, where graphene can produce other gases which are toxic. On the contrary, the progress resulting from the Hummers method can be viewed from reducing the production of toxic gases, reducing work accidents resulting from hazardous compounds, and reducing the creation of toxic gas evolution. The modified Hummers method synthesizes graphene from graphite oxide using oxidizing compounds such as sulfuric acid at a concentration of 98%, nitric acid and potassium permanganate. The results obtained from this method were the level of effectiveness of the oxidation was influenced by the ratio between graphite oxide in the product or by the ratio between carbon and oxygen. The optimal ratio for oxidation to occur was with a carbon to carbon ratio of 2.1 to 2.9. The characterization of the microwave absorption properties, structure, and functional groups of the graphene oxide (GO) was conducted using XRD (X-Ray Diffraction), FTIR (Fourier Transform Infrared), and VNA (Vector Network Analyzer). X-Ray Diffraction (XRD) was used to determine the structure of a crystal, to identify the phase and to determine the size of the crystal being tested [15]. Fourier Transform Infra Red (FTIR) was used to determine the functional groups present in graphene oxide. Vector Network Analyzer (VNA) was used to analyze the absorption properties

of a material against microwaves at certain frequencies. The characterization of the VNA will display the value of the Reflection Loss (RL) which then the value of this RL will be used to determine the properties of the microwave absorber.

The research involves several stages, namely: preparation stage, sugarcane bagasse pre-treatment stage, carbon activation stage, GO synthesis stage, sonication and neutralization stage of GO, GO characterization stage, data collection stage, and data analysis stage. The research flowchart is shown in Figure 1.

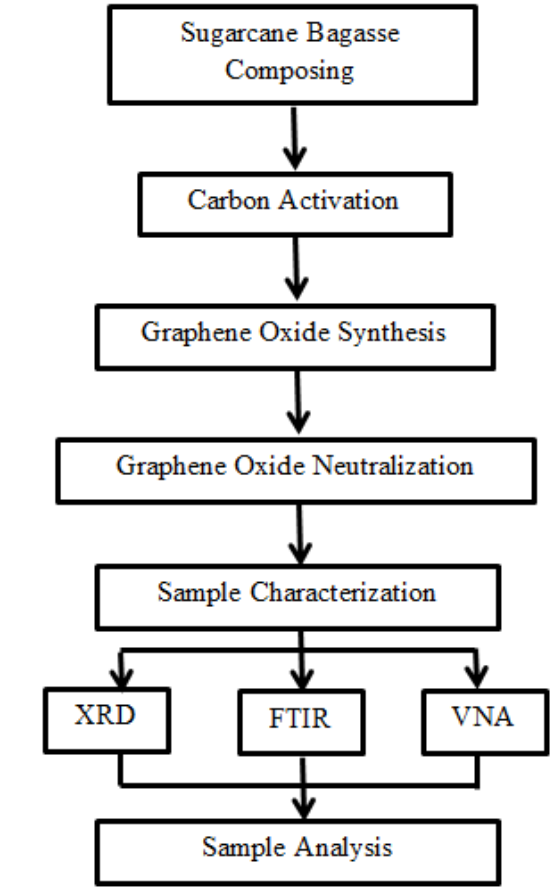

Fig 1. The Research Flowchart

In this stage, the Hummers method was modified to reduce the generation of toxic gas evolution, thus eliminating the use of $NaNO_3$ compound in the modified Hummers method. The modified Hummers method involved excluding $NaNO_3$, increasing the amount of $KMnO_4$, and performing the reaction in a 9:1 (by volume) mixture of H_2SO_4 / H_3PO_4. The increased use of KMnO4 in the modified Hummers method led to the formation of a new compound, H_3PO_4 [16].

The temperature variations used were 300°C, 350°C [17], 400°C, and 450°C [18] in order to observe the influence of the furnace variation from sugarcane bagasse waste on the microwave absorption properties of GO. The duration of the sugarcane bagasse oven process is 60 minutes at a temperature of 100°C. The furnace process takes 30 minutes. The concentration of H_2SO_4 is 98 wt%, the concentration of H_2O_2 is 30 wt%, and the concentration of NaOH is 2N. The duration of the centrifugation process and stirring process for each stage may vary. The pH of the GO is approximately 7. The GO is oven-dried at 60°C for 12 hours. The composition of materials used in each stage may vary. For VNA testing, the mold size is 3 cm x 1.5 cm with a thickness of 2 mm.

III. RESULTS AND DISCUSSION

The XRD testing data on the graphene oxide (GO) samples consists of infrared (IR) spectra that represent the relationship between scattering angle (2θ) and peak spectrum intensity (I). The number of intensity counts hitting the atoms increases as the arrangement of atoms becomes longer and more orderly, resulting in more diffraction counts received by the detector and forming sharp and pointed intensities. The result characterization of XRD is shown in Figure 2.

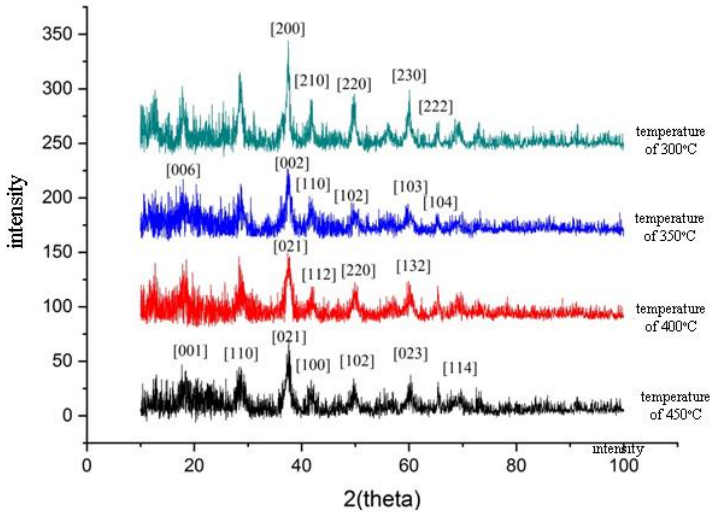

Fig 2. XRD Characterization Results of Graphene Oxide at Various Temperatures (300°C, 350°C, 400°C, 450°C)

Based on Figure 2, the graph of Miller index identification for peak variations at a temperature of 300°C is associated with emerging phases, namely (200), (210), (220), (230), and (222). Based on the displayed graph pattern, the calculated crystal size using the Scherrer equation is 18.98051563 nm. The XRD test results for the 350°C variation have Miller index identification using Origin software, revealing the emergence of phases (006), (002), (110), (102), (103), and (104). Based on the obtained ICDD data, the lattice parameters obtained according to Bravais lattice are $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$, which corresponds to a hexagonal crystal system. The calculated crystal size using the Scherrer equation is 25.93692581 nm. The XRD analysis results at 400°C, using Origin software for Miller index identification, indicate the emergence of phases (021), (112), (220), (132), and (041). Based on the obtained ICDD data, the lattice parameters obtained according to Bravais lattice are $a \neq b \neq c$, and the values of $\alpha = \beta = \gamma = 90°$, resulting in an orthorhombic crystal system. The calculated crystal size using the Scherrer equation is 21.84037863 nm. The XRD analysis results at 450°C, using Origin software for Miller index identification, show the emergence of phases (001), (110), (021), (100), (102), (113), (023), (132), (114), (041), and (240). Based on the obtained ICDD data, the lattice parameters obtained according to Bravais lattice are $a \neq b \neq c$, and the values of $\alpha = \beta = \gamma = 90°$, resulting in an orthorhombic crystal system. The calculated crystal size using the Scherrer equation is 40.5267076 nm.

The testing of graphene oxide using FTIR was conducted to identify the functional groups formed in graphene oxide. The FTIR characterization results were processed using Origin software, displaying the relationship between wavenumber (cm-1) on the X-axis and transmittance (%) on the Y-axis. The spectrum of infrared waves of graphene oxide falls within the wavenumber range of (500 - 4000) cm-1 as shown in Figure 3.

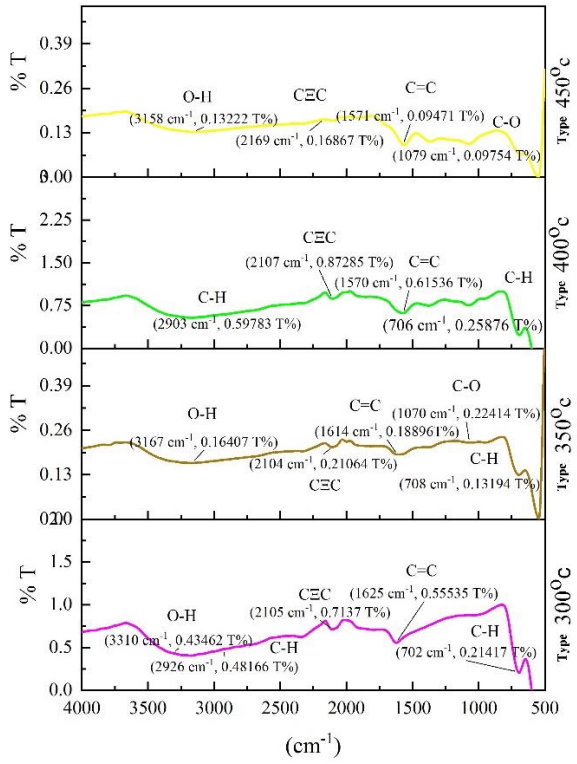

Fig 3. FTIR Characterization Results of Graphene Oxide at Various Temperatures (300°C, 350°C, 400°C, 450°C)

In Figure 3, several absorption peaks can be observed, displayed from the results of testing using FTIR. Some of these peaks correspond to combinations of functional groups like C=C, C-O, C≡C, C-H, and O-H. Graphene oxide can form bonds such as C=O, C-H, COOH, and C-O-C with carbon atoms in its layers. At each temperature variation, they each exhibit functional group bonds that align with the structure of graphene oxide's functional groups. The C=C functional group appears at wavenumbers of 1600 - 1680 cm-1, involving compounds like alkenes and aromatic rings. The C-O functional group appears at wavenumbers of 890 - 1300 cm-1, representing compounds such as alcohols, ethers, carboxylic acids, and esters. The O-H functional group appears at wavenumbers of 3000 - 3640 cm-1, indicating compounds like alcohols and hydroxides. The C≡C functional group appears at wavenumbers of 2100 - 2260 cm-1, corresponding to compounds known as alkynes, while the C-H functional group appears at wavenumbers of 610 - 860 cm-1, associated with compounds like aromatic rings and alkynes (Nandiyanto, A.B.D., et al., 2019). Graphene Oxide (GO) or graphite acid is a composite compound of carbon (C), hydrogen (H), and oxygen (O) acquired through a strong oxidation process of graphite (Sukmawati, 2018). This confirms the presence of graphene oxide layers, substantiated by the bonds formed between Carbon (C), Hydrogen (H), and Oxygen (O).

The testing of GO using VNA was conducted to determine the absorption properties of a material towards microwaves. The graph depicting the results of the GO test using VNA shows the relationship between Reflection Loss (RL) on the Y-axis and frequency (f) on the X-axis. The frequency values used are within the range of 8-12 GHz (X-band frequency), as shown in Figure 4.

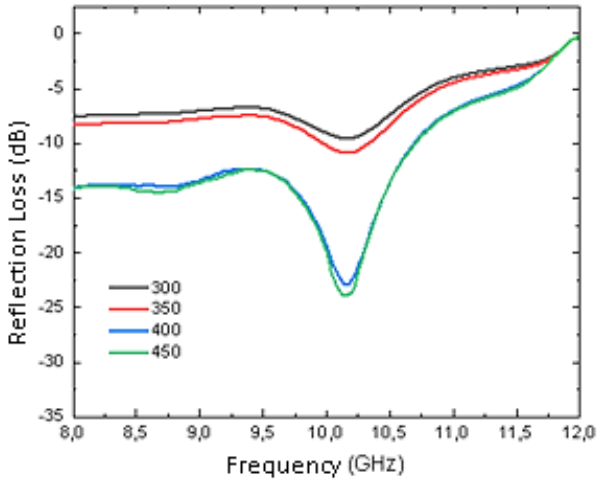

Fig 4. VNA Characterization Results of Graphene Oxide at Various Temperatures (300°C, 350°C, 400°C, 450°C)

Not only the parameters of reflection loss, absorption coefficient, and absorption bandwidth can affect the absorption properties of a material, but also the density and thickness of the material [19]. A denser material exhibits greater absorption capacity because the grains are closer together, leaving no empty spaces for wave transmission. Conversely, a looser arrangement results in lower absorption capacity. Similarly, the thickness of the material also affects its absorption properties, as a thicker material allows for longer reflection within the material, resulting in lower transmitted power. Therefore, the density and thickness of the material must be consistent to ensure its absorption properties are not affected [20].

Table 1. GO Absorption Values

GO Variations (°C)	Frequency (GHz)	*Reflection Loss* (dB)	Absorption Coefficient (%)
300	10.16	-954	66.66
350	10.16	-10.89	71.46
400	10.16	-22.89	92.83
450	10.16	-23.94	93.65

Based on the Table 1, it is found that GO 450 exhibits good microwave absorption properties. This is because it has a small reflection loss value (-23.94 dB), a high absorption coefficient (93.65%), and a wide absorption bandwidth (1.13 GHz). Reflection loss is an indicator of the amount of electromagnetic energy lost after hitting a material, as the energy is absorbed by the material [21]. The higher the minimum reflection loss value, the better the absorption capability of the material. The reflection coefficient is the ratio of the reflected wave to the incident wave. If the reflection coefficient of a sample is 0, it means that the input impedance is equal to the output impedance, indicating that no waves are reflected by the material, but rather the electromagnetic waves that hit the sample are absorbed. The absorption bandwidth refers to the range of frequencies in which a material can absorb microwaves effectively. The result characterization of VNA is shown in Table 2.

Table 2. GO Absorption Bandwidth

GO Variations (°C)	Frequency (GHz)	*Reflection loss* (dB)	Absorption Band (GHz)	Absorption Bandwidth (GHz)
300	10.16	-9.54	9.61-10.63	1.02
350	10.16	-10.89	9.49-10.51	1.02

400	10.16	-22.89	9.62-10.72	1.10
450	10.16	-23.94	9.61-10.74	1.13

Based on the obtained results, GO 300º, GO 350º, GO 400º, and GO 450º exhibit different values for reflection loss, absorption coefficient, and absorption bandwidth. This is due to the influence of the sintering temperature. This influence is reflected in the changing values of reflection loss, absorption coefficient, and absorption bandwidth with increasing sintering temperature. Higher sintering temperatures lead to larger absorption coefficients and wider absorption bandwidths, while reflection loss values decrease. Sintering is a process of compacting a collection of powders at high temperatures, aiming to densify the printed material. The sintering process affects the formation of crystal phases and the growth structure of crystals. Higher sintering temperatures accelerate the formation of crystals. GO 450 exhibits the smallest reflection loss value, the largest absorption coefficient, and the widest absorption bandwidth. A small reflection loss value corresponds to a large absorption coefficient and a wide absorption bandwidth, indicating that GO 450 can be considered as a material with good microwave absorption properties.

IV. CONCLUSION

Graphene oxide is a monolayer of carbon atoms dotted with oxygen functional groups. Abundant and unused bagasse is a promising candidate as a carbon source for the manufacture of graphene oxide because of its high carbon content. The Hummer Modification Method is a convenient and simple wet chemical process that can be presented for synthesizing graphene oxide from bagasse. Characterization using XRD, FTIR, and VNA showed that Graphene Oxide has been successfully produced from bagasse. Graphene oxide plays an important role in today's scientific and technological advances. GO can be applied to various things, such as seawater desalination, batteries, anti-bacterial plasters, wall paints, field effect transistors (FET), and in the biomedical field. Many studies continue to report on advanced applications of graphene oxide illustrating future advances in graphene oxide-based technologies.

V. ACKNOWLEDGMENTS

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