



The Effect of Magnetic Stirring Duration and Ascorbic Acid Concentration on the Yield of Reduced Graphene Oxide Isolated from East Kalimantan Bituminous Coal

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ABSTRACT: East Kalimantan bituminous coal has a carbon composition of 70.24%, indicating a crystal structure of graphite layers. This makes it a viable material for creating reduced graphene oxide (r-GO), which has multiple advantages in various properties and can be employed in numerous technological applications. RGO is obtained by nearly eliminating oxygen functional groups in graphene oxide (GO) through sonication for 3 hours at pH 4. The yield with the lowest value at a 10% concentration of ascorbic acid and 50 minutes of magnetic stirring was selected as optimal. To characterize the resulting product, FTIR was utilized and revealed that O-H (84.21%), C=C (63.04%), and C-O-C (61%) had the highest %T. Technical abbreviations were explained upon first use. Energy-dispersive X-ray (EDX) analysis demonstrated a 90.6% increase in carbon content from 40.159% in GO to 76.554% in r-GO. In parallel, oxygen content decreased from 40.973% in GO to 17.551% in rGO, marking a 57.16% decrease. The morphology of the resulting rGO closely resembled the reference. Additionally, rGO exhibited a C:O ratio of 4.378, surpassing the C:O ratio of GO, which was 1.02. RGO density and pH value were 1.45 g/cm³ and 2, respectively.

KEYWORDS: Ascorbic Acid; Bituminous Coal; Graphene Oxide; Reduced Graphene Oxide; Magnetic Stirrer

INTRODUCTION

Coal is a natural resource that is abundantly available in Indonesia, accounting for approximately 2.2% of the total global coal reserves (Santoso, 2018). Information obtained from the East Kalimantan Provincial Mining Office in 2015 suggests that the region has approximately 50.12% of the total coal reserves in Indonesia, estimated at approximately 62.80 billion tons. East Kalimantan is the region within Kalimantan that possesses the most significant coal resources (Pratomo et al., 2020). Coal forms from the deposition of plant material in swamps under low-oxygen conditions to hinder decay. This geological process takes hundreds of years and yields a coal structure comprising hydrocarbon molecules, predominantly of the chemical element carbon, alongside nitrogen, oxygen, and sulfur elements. Coal varieties are classified based on their carbon content and include peat, lignite, sub-bituminous, bituminous, and anthracite. In Indonesia, coal is categorized into different qualities such as sub-bituminous (26.60%), bituminous (14.40%), and anthracite (0.40%). The majority of the remaining coal belongs to the lignite category (58.60%), which is considered to be of relatively young age and low quality (Yustanti, 2012). Coal from Anugerah Bara East Kalimantan Ltd. is a type of bituminous coal known for its soft texture. It is commonly used as a fuel source in industry. The composition of bituminous coal found in East Kalimantan is 70.24% elemental carbon (C). It has a graphite crystal structure with layers of carbon that are now referred to as graphene. Bituminous coal is advantageous due to its high carbon content, low moisture content, and volatility value. Although its heating value is not the highest, it is second only to anthracite coal. Bituminous coal exhibits low amounts of water, sulfur, and ash content. Its flammability and ability to sustain flame over extended periods transpire when its particles undergo combustion at a smaller size than the chunks of coal located in mines (Huda et al., 2017).

Graphite is a type of carbon that is crystalline, black, and has a soft texture (Dai et al., 2012). Graphene is a constituent of graphite, and therefore, many similarities exist between the two materials. Graphene oxide (GO) and its reduced form (rGO) possess unique properties that resemble those of graphene, suggesting they have significant potential in various fields (Yan et al., 2020). Reduced graphene oxide (rGO) is produced by almost completely removing oxygen functional groups, resulting in a material with nearly identical mechanical, electrical, and optical properties to graphene. This makes it a versatile and easily applicable material for various technological uses (Rowley-Neale et al., 2018). Reduction from graphene oxide (GO) to reduced graphene oxide (r-GO) can be accomplished utilizing various methods, such as several reducing agents (Chua & Pumera, 2016), thermal treatment (Jakhar et al., 2020), laser radiation (Longo et al., 2017), or a bacterial approach (Utkan et al., 2019). Although hydrazine is a commonly



employed reducing agent, it poses severe safety hazards due to its explosive nature and can result in the production of rGO with low quality when nitrogen is added. In addition, the use of sulfuric acid to synthesize graphene oxide is often harmful to the environment and toxic. To provide a more environmentally friendly alternative, ascorbic acid (AA) was discovered as an alternative reducing agent for the conversion of GO into rGO (Go et al., 2018). One method for synthesizing rGO from graphene oxide is through the use of sonication or mechanical stirring utilizing a magnetic stirrer (Emiru & Ayele, 2017). The magnetic stirrer technique applies environmentally friendly principles, including minimizing waste resulting from solvent usage in the manufacturing process of rGO. The rapid rotation of the magnetic stirrer has a significant impact on the reduction of particle size since it distributes energy uniformly throughout the solution. Consequently, this leads to particles having more consistent sizes.

Graphene oxide is derived from graphite by adjusting pH with the addition of HCl, assisted by sonication. The study conducted by (Mutrofin et al., 2021) revealed that pH 4 provided the most favorable conditions for the production of graphene oxide. The purpose of this study is to employ green chemistry techniques, implementing ascorbic acid and magnetic stirring, to generate reduced graphene oxide. The study investigates the impact of adjusting the concentration of ascorbic acid and the duration of magnetic stirring on the production of reduced graphene oxide obtained from bituminous coal in East Kalimantan. The aim is to attain the optimum yield.

METHODS

This research aims to objectively report on the mechanical production of reduced graphene oxide (rGO) using magnetic stirrers, specifically in isolating graphene oxide (GO) from coal. The study investigates the effects of varying concentrations of ascorbic acid and stirring time on the efficiency of magnetic stirrers in achieving the optimal production of rGO from coal. The obtained results hold promise for future application of rGO.

Tools and Materials

The following tools were utilized in the experiment: 100 mL, 500 mL, and 1000 mL beakers, a 100 mL measuring cup, 10 mL and 100 mL volumetric flasks, a watch glass, 100 mL and 500 mL Erlenmeyer flasks, a funnel, a glass stirring rod, a dropper pipette, measuring pipettes, a 10 mL volume pipette, a spatula, a porcelain cup, 150 mesh and 200 mesh sieves, a mortar and pestle, an analytical balance, and an oven. The materials utilized include 11-micron Hawach filter paper, desiccator, plastic wrap, aluminum foil, sample bottle, magnetic stirrer, hotplate, pH indicator, pycnometer, Ultrasonic Cleaner Delta D68H 2L, Fourier-Transform Infrared Spectroscopy spectrophotometer type Varian fts 1000, and Scanning Electron Microscope Thermo Scientific. Bituminous coal from Anugerah Bara East Kalimantan Ltd., as well as 10%, 20%, and 30% solutions of ascorbic acid, 0.1 M HCl p.a solution, n-hexane, toluene, and aquadest were utilized in the experiment.

Research Procedure

Coal Sample Preparation

Sample preparation begins with bituminous coal obtained from Anugerah Bara in East Kalimantan Ltd. The coal is ground and pulverized using a porcelain grinder, then sieved using 150 mesh and 200 mesh sievers. The coal used is the portion that passes through the 150 mesh sieve and is retained on the 200 mesh sieve, which is then referred to as the 200 mesh coal sample. A total of 150 g of 200 mesh samples are prepared, heated in a 40°C oven for 10 hours, and then left to stand in a desiccator. The sample was rinsed with distilled water at a ratio of 1:5 and stirred on a hotplate (without heating) using a magnetic stirrer set to a speed of 6-7 on the scale (1500 rpm) for three hours. It was then filtered using 11-micron Hawach filter paper until the filtrate was clear of impurities. The resulting material was transferred to a porcelain container and dried in an oven at 40°C for 10 hours. Finally, the material was placed in a desiccator.

Preparation of Graphene Oxide from Coal Samples

The coal sample was weighed to 5.0 g and placed in a 500 mL Erlenmeyer flask. Then, 250 mL of distilled water was added. The initial pH was measured using pH indicator paper. 0.1 M HCl was added until the pH of the solution reached 4. The sample solution was sonicated for three hours with a 30-minute interval every hour. Finally, the solution was filtered using 11-micron Hawach filter paper. The yield from the filtration was then placed on a porcelain cup and dried in an oven at 40°C for 10 hours, then allowed to stand in a desiccator for 15-20 minutes. The obtained graphene oxide yield was transferred into a sample bottle, and characterization was carried out using a pycnometer, pH test, solubility test, FTIR and SEM-EDX.



Preparation of Reduced Graphene Oxide (rGO) from Graphene Oxide with Variation of Ascorbic Acid Concentration

This study employs the reduction method to produce rGO. The synthesis of rGO is carried out by adding a reducing agent, ascorbic acid, which functions to remove oxides during the reduction process. The preparation of rGO involves taking a 1.0 g sample of graphene oxide and adding 50 mL of aquedest to a 100 mL beaker. The sample solution was stirred using a magnetic stirrer for 2 hours, with 30-minute intervals every hour. Ascorbic acid was added in varying concentrations of 10%, 20%, and 30% in a 1 mL volumetric flask. The solution was then stirred again for 30 minutes using a magnetic stirrer. Subsequently, the solution was filtered using 11-micron Hawach filter paper. The filtered yield was then placed in a porcelain cup and dried in an oven at 50°C for 24 hours. Finally, it was allowed to stand in a desiccator for 15-20 minutes. The yield from each concentration variation was weighed, and the yield with the lowest weight was characterized using an FTIR spectrophotometer.

Preparation of Reduced Graphene Oxide (rGO) from Graphene Oxide with Variation of Magnetic Stirring Time

To prepare rGO, start with 1.0 g of graphene oxide in a 100 mL beaker and add 50 mL of distilled water. Stir the solution with a magnetic stirrer for 2 hours, with 30-minute intervals every hour. Then, add ascorbic acid at the optimum concentration and stir again for 10, 30, and 50 minutes. Finally, filter the solution using 11 micron Hawach filter paper. The filtered yield was placed in a porcelain cup and dried in an oven at 50°C for 24 hours. It was then allowed to stand in a desiccator. The yield of each variation was weighed and characterized using FTIR. The optimum reduced graphene oxide was further characterized using a pycnometer, pH indicator, solubility test, and SEM-EDX.

Characterization

Characterization of graphene oxide and reduced graphene oxide involved tests for density, solubility, and pH, alongside analysis from a FT-IR spectrophotometer and SEM-EDX. Technical term abbreviations were explained when first used.

RESULTS AND DISCUSSION

Coal Sample Preparation

The study utilized bituminous coal obtained from Anugrah Bara Kalimantan Timur Ltd. Coal sample preparation aimed to facilitate research before analysis. The coal solids were initially 5-15 mm in size and black in color. To obtain a finer powder, the coal was pulverized using a porcelain grinder. The coal is pulverized and then sieved through a 150 mesh and 200 mesh sieve to ensure uniform size. The resulting coal that passes through the 150 mesh sieve and is retained in the 200 mesh sieve is referred to as the 200 mesh or 74000 nanometer coal sample. The coal samples are then washed with aquaquin in a ratio of 1:5 and stirred on a hotplate (without heating) using a magnetic stirrer with a scale speed of 6-7 (1500 rpm) for three hours. The purpose of washing coal is to remove impurities. Next, filter the coal using 11-micron Hawach filter paper until the filtrate is clear of impurities. Transfer the filtrate to a porcelain container and dry it in an oven at 40°C for 10 hours to remove inorganic minerals without damaging the carbon in the coal. Finally, transfer the coal samples to sample bottles for use.

Preparation of Graphene Oxide from Coal Samples

(Mutrofin et al., 2021) conducted research on the manufacture of Graphene Oxide (GO) from bituminous coal. They found that GO can be obtained at optimum conditions with a pH setting of 4. The process begins by weighing five grams of activated coal sample and placing it in a 500 mL Erlenmeyer flask. Then, 250 mL of distilled water is added and the initial pH of the solution is checked using pH indicator paper. The reaction conditions are adjusted by adding 0.1 M HCl to reach a pH of four. Acids, such as HCl (hydrochloric acid), serve as chemical activation agents that can stimulate changes in coal structure. This helps to increase the reactivity and porosity of coal, resulting in the release of large amounts of volatile and non-volatile compounds (Delmifiana, 2013). The activation process was followed by sonication of the solution for three hours at 30-minute intervals every one hour to enhance the activation and dispersion of particles in the solution. According to the literature, sonication time can affect particle size because the collisions between the particles in the solution become longer, resulting in more homogeneous and smaller particles (Zhu, 2014). The solution was filtered using 11 micron Hawach filter paper to remove unwanted particles. The filtered yield was then dried in an oven at 40°C for 10 hours and stored in a desiccator for 15-20 minutes. Drying at 40°C was chosen to minimize errors and suboptimal results, as air drying or drying at higher temperatures can cause oxidation and damage to the coal structure (Nadia et al., 2014). The graphene oxide produced was transferred to a sample bottle for characterization. The characterization



process included using a pycnometer, conducting a solubility test, measuring pH, analyzing with FTIR, and examining morphology with SEM-EDX.

Preparation of Reduced Graphene Oxide (rGO) from Graphene Oxide with Variation of Ascorbic Acid Concentration

The reduction method is utilized in this stage to produce rGO by adding ascorbic acid as a reducing agent. Ascorbic acid, also known as vitamin C, is a non-toxic natural antioxidant and reducing agent that can be used to prepare reduced graphene oxide through the reduced graphene oxide method (Pei & Cheng, 2012). AA is non-toxic as it does not release harmful gases during the reaction process, making it environmentally friendly. To prepare the sample, 1 gram of GO was stirred with 50 mL of academy for 2 hours using a magnetic stirrer. Ascorbic acid was then added with concentrations of 10%, 20%, and 30%, respectively, and stirred for an additional 30 minutes. Ascorbic acid serves as a reducing agent in the preparation of reduced graphene oxide (rGO) by eliminating groups such as COOH, OH, and O. The solution was filtered using 11 micron Hawach filter paper and the resulting filter was dried in an oven at 50°C for 24 hours. The FTIR spectrophotometer was used to analyze the lowest yield and identify any structural changes in graphene after reduction, as well as the effect of varying ascorbic acid concentration. **Table 1** shows the yield results based on variations in ascorbic acid concentration. The average yield of rGO was 96.7% at a concentration of 10% AA, 102.6% at a concentration of 20% AA, and 106.2% at a concentration of 30% AA. These results suggest that the yield increases with higher concentrations of AA.

Table 1. Yield of rGO with Variation of Ascorbic Acid Concentration

Repetition	AA 10%	AA 20%	AA 30%
1	95,72	102,59	107,01
2	97,81	101,49	105,5
Average	96,7	102,6	106,2

The optimal concentration of 10% AA was selected based on the assumption that impurities in GO are effectively reduced at this concentration, allowing inorganic minerals to be filtered out. Yields obtained at 20% and 30% AA concentrations were above 100%, indicating a reversible reaction where AA forms a complex with impurities, leading to an increase in yield.

Preparation of Reduced Graphene Oxide (rGO) from Graphene Oxide with Variation of Magnetic Stirring Time

After determining the optimal concentration of AA, the preparation of rGO was carried out by varying the length of magnetic stirring. The process began by mixing one gram of the GO sample in a 100 mL beaker with 50 mL of distilled water. Ascorbic acid was then added at the optimal concentration and stirred for 10, 30, and 50 minutes. The mixture was stirred for 2 hours with 30-minute intervals. Finally, the solution was filtered using 11-micron Hawach filter paper. The yield of each variation was dried in an oven at 50°C for 24 hours and then left to stand in a desiccator. Afterward, FTIR was used to characterize the yield. The optimum Reduced Graphene Oxide was further characterized using a pycnometer, pH indicator, solubility test, and SEM-EDX.

The method employed in the preparation of reduced graphene oxide was a mechanical method using a magnetic stirrer. The speed of the magnetic stirrer affects particle size reduction by equalizing the energy received by all parts of the solution, resulting in more homogeneous particle sizes (Taurina et al., 2017). Increasing the speed and length of stirring decreases particle size and breaks bonding groups. Longer stirring times result in smaller particle sizes due to the breaking of more oxygen bonds. Increasing the rotation speed of the magnetic stirrer leads to a higher intensity of contact between the solvent molecules and the particles, resulting in smaller particles (Nandiyanto et al., 2019). **Table 2** shows the yield results for different magnetic stirring durations.

Table 2. Yield of rGO with Variation of Magnet Stirring Time

Repetition	10 minutes	30 minutes	50 minutes
1	95,93	95,72	96,74
2	96,88	97,81	97,78
Average	96,4	96,7	97,2

Based on the table, it is evident that every different stirring time resulted in yields that are comparable and below 100%. Subsequently, a T test was performed to determine whether there were any significant differences in the data. The outcomes of the T test discovered that the T count was lower than the T table, indicating that there was no significant variation in the data. Consequently, it can be concluded that every time variation has the potential to be considered the optimal time. FTIR analysis was conducted on each variation to determine the optimal time for reducing GO to rGO using AA reducing agent with a concentration of 10%. The analysis of functional groups indicated that a stirring time of 50 minutes was the most effective. The selection of 50 minutes as the optimal time is based on the results of characterization using an FTIR spectrophotometer. The highest %T increase was observed for wave numbers $3550\text{-}3200\text{ cm}^{-1}$ (O-H alcohol), $3700\text{-}3100\text{ cm}^{-1}$ (O-H water), $2950\text{-}2850\text{ cm}^{-1}$ (C-H alkyl), and $1700\text{-}1500\text{ cm}^{-1}$ (C=C aromatic), as well as wave number regions $900\text{ cm}^{-1}\text{-}400\text{ cm}^{-1}$, which are characteristic frequencies for O-metal vibrations.

Table 3. Tabulation of %T FTIR GO and rGO: Variation of Magnetic Stirring Time

Functional Group	Wave Number (cm^{-1})	%T GO	%T rGO 10'	%T rGO 30'	%T rGO 50'
O-H	3550-3200	82.31	80.78	77.40	84.21
O-H	3700-3100	81.06	79.81	76.50	81.85
C-O-C	1250-1050	60.09	56.58	52.51	61.00
M-O	900-400	15.70	16.80	14.33	18.87

Reduction Reaction of GO to rGO with Ascorbic Acid

Ascorbic acid, also known as vitamin C, is a natural and safe antioxidant and reducing agent that can be utilized in creating rGO through the reduced graphene oxide method, as outlined by (Pei & Cheng, 2012). By utilizing reducing agents, groups like COOH, OH, and O can be effectively removed. L-Ascorbic Acid represents the reduced form, whilst Dehydroascorbic Acid represents the oxidized kind, with ascorbic acid frequently taking both unstable forms. Research suggests that ascorbic acid can produce reduced graphene oxide (rGO) within a similar timeframe and with comparable electrical conductivity as GO reduced using hydrazine (Fernández-Merino et al., 2010). The process comprises two primary reactions: reduction of epoxy groups as depicted in **Figure 1a** and reduction of hydroxyl groups as shown in **Figure 1b**. Protonation of GO reactive groups takes place, which is then followed by the $\text{S}_{\text{N}}2$ reaction step, where nucleophile agents attack the carbon. The outcome is the synthesis of rGO, accompanied by the production of dehydroascorbic acid and water as by-products as presented in **Figure 2**.

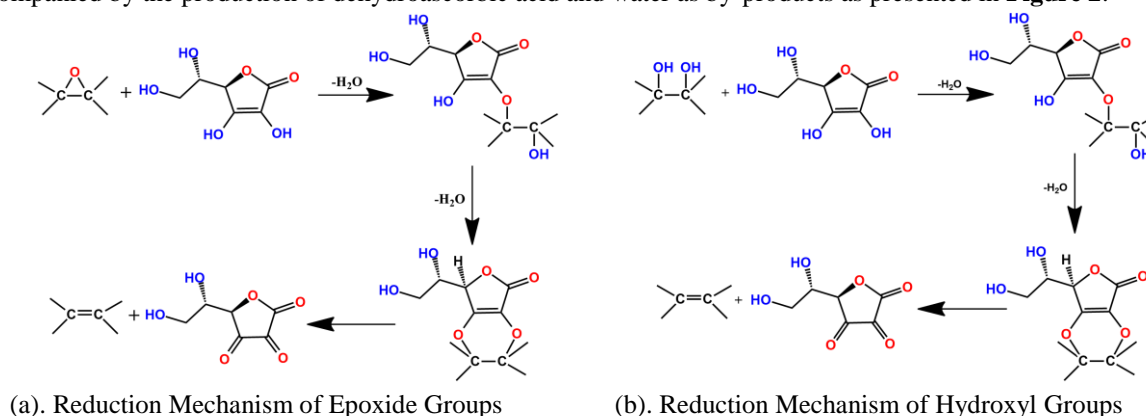


Figure 1. Reduction Mechanism of (a). Epoxide Groups and (b). Hydroxyl Groups (Gao et al., 2010)

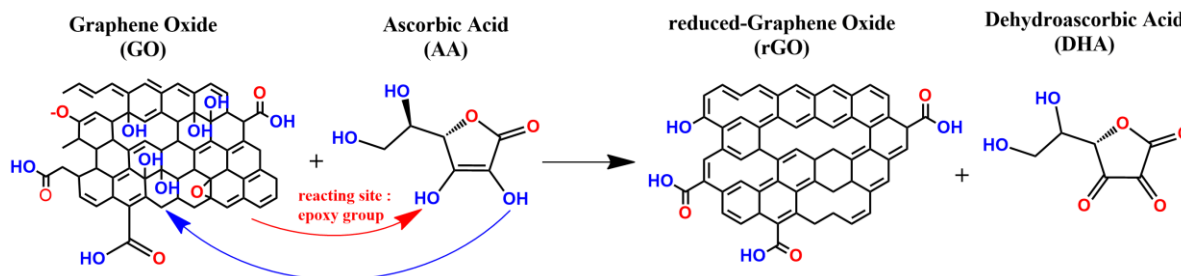


Figure 2. Reduction Mechanism of GO with Ascorbic Acid (Palomba et al., 2022)

Characterization

Characterization with Fourier Transform Infrared Spectrophotometer

Fourier Transform Infrared is an analytical technique used to characterize samples in various forms, including liquids, solutions, powders, films, fibers, and gases. The principle of this FT-IR spectrophotometer is that infrared (IR) radiation interacts with the molecular atoms in the sample, causing them to vibrate and produce a unique energy transmission (Bakatula et al., 2018). Each type of functional group has its own specific and distinctive infrared absorption bands. FTIR measurements are conducted in the mid-infrared region, specifically at wave numbers $4000\text{-}200\text{ cm}^{-1}$ (Andrijanto et al., 2016)

The purpose of FT-IR analysis is to identify the functional groups present in GO and rGO samples. The FT-IR spectra of the GO and rGO samples showed similar results. In general, GO contains oxygen functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and epoxy (C-O-C). Even after the reduction process, some oxygen groups may still be present on rGO, albeit in smaller quantities than GO. Functional groups that may remain on rGO include hydroxyl (OH) and epoxy (C-O-C). FT-IR characterization of GO and rGO samples revealed hydroxyl absorption peaks at wave numbers $3550\text{-}3200\text{ cm}^{-1}$, epoxy functional group absorption peaks at wave numbers $1250\text{-}1050\text{ cm}^{-1}$, and aromatic C=C functional group absorption peaks at wave numbers $1700\text{-}1500\text{ cm}^{-1}$ (Wijayanto & Bayuseno, 2014). **Figure 3** presents the results.

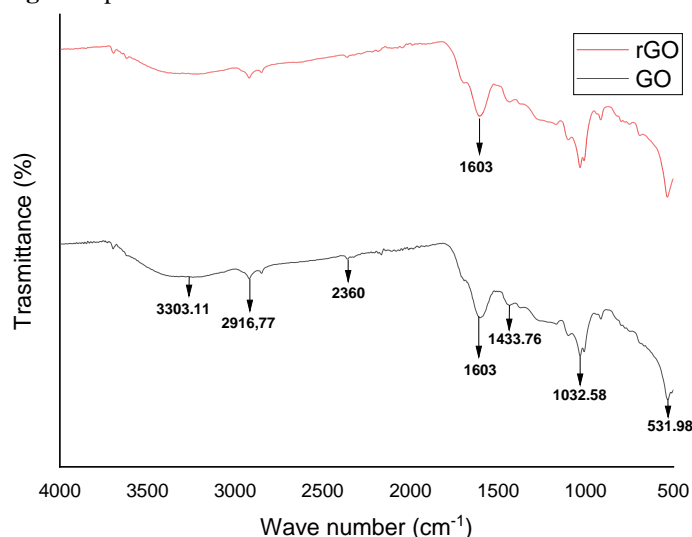


Figure 3. FTIR Spectra of Graphene Oxide (GO) and Reduced Graphene Oxide (rGO)

Figure above displays the FTIR test results for GO and rGO. The GO spectrum exhibits a peak at 531 cm^{-1} , which is caused by M-O attraction. Additionally, there is a peak at 1032 cm^{-1} , which shows C-O-C bending. At 1603 cm^{-1} , there is a vibration caused by the presence of aromatic C=C groups. The broad peak at 3303 cm^{-1} indicates the vibration of the O-H alcohol group. In contrast, the spectrum of rGO indicates the reduction of oxygen groups on GO by ascorbic acid (AA), as evidenced by the absence of the aforementioned peaks. The spectra above indicate that the peaks at 1032 and 3303 cm^{-1} have been reduced, suggesting the removal of some oxygen functional groups on GO. The sharp peak at 1603 cm^{-1} on rGO indicates a strong aromatic C=C functional group.

However, some oxygen functional groups still remain on the surface of rGO after the reduction process. The FTIR results are similar to the research conducted by (Andrijanto et al., 2016), which highlights the difference between GO and rGO. The GO spectrum shows a peak at 1066 cm^{-1} , indicating the presence of C-O attraction, and peaks at 1288 cm^{-1} and 1587 cm^{-1} , representing O-H attraction from C-OH and water groups in the material, and C-O-C and C-OH vibrations, respectively. The material exhibits a carbonyl group at 1724 cm^{-1} and a broad peak at 3448 cm^{-1} , indicating the O-H attraction vibration of the C-OH group and water. In the rGO spectrum, these peaks are less intense, suggesting the removal of most oxygen functional groups in GO through reduction using ascorbic acid (AA). The peak at 1605 cm^{-1} in rGO indicates a strong recovery of the sp^2 structure, suggesting a return to a more reduced state of graphene.

Characterization with Scanning Electron Microscope (SEM) & Energy Dispersive X-ray (EDX)

The morphology of graphene oxide (GO) and reduced graphene oxide (rGO) was characterized using SEM and EDX analysis to detect the elemental composition and topography of the materials. **Figure 4a** shows the flake-like and irregular morphological structure of GO. The SEM results indicate that the structures of GO and rGO display irregular, randomly clustered, tightly connected, and overlapping sheet structures (Bychko et al., 2022). After reduction with ascorbic acid using a magnetic stirrer, the GO surface underwent a change in morphology resulting in the formation of layers and a decrease in the distance between them, as shown in **Figure 4b**. This was due to the removal of oxygen groups on the GO surface (Hsieh et al., 2013).

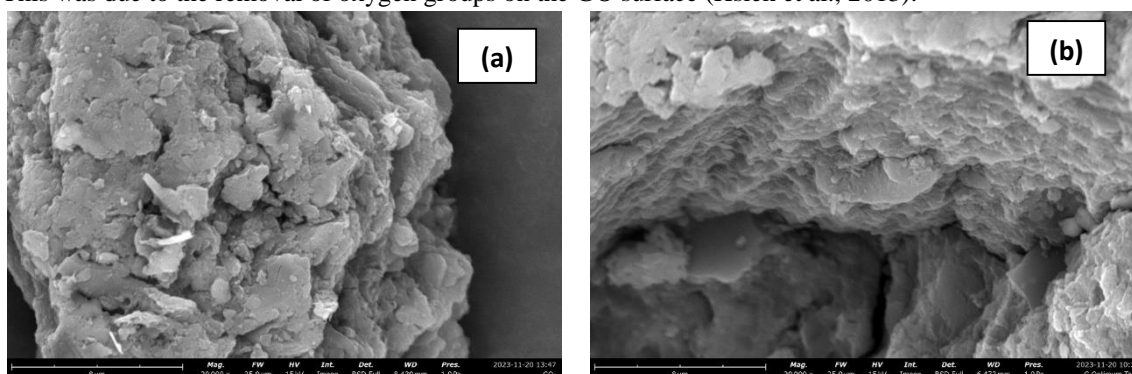


Figure 4. SEM Morphology Results of (a) GO and (b) rGO at 20,000x Magnification

The treatment of Graphene Oxide with Ascorbic Acid and magnetic stirring yields positive results for its use as raw material in the manufacture of Reduced Graphene Oxide. This is achieved through the reduction method, which reduces the oxygen content and removes impurities. **Table 4** shows the average carbon-oxygen ratio (C/O) of GO, while **Table 5** shows the same for rGO. The data was collected from three different spots.

Table 4. Carbon-Oxygen (C/O) ratio for GO

GO				
Element	Spot 1	Spot 2	Spot 3	\bar{x}
C	39.255	50.468	30.755	
O	41.544	34.142	47.234	
C/O	0.945	1.478	0.651	1.02

Table 5. Carbon-Oxygen (C/O) ratio for rGO

rGO				
Element	Spot 1	Spot 2	Spot 3	\bar{x}
C	75.854	79.323	74.985	
O	17.246	17.093	18.314	
C/O	4.398	4.641	4.094	4.378

The results of the calculations show that the average carbon content increased by 90.6% from GO (40.159%) to rGO (76.554%). Additionally, the oxygen content decreased by 57.16% from GO (40.973%) to rGO (17.551%). As a result, the C:O ratio of rGO increased to 4.378, compared to the C:O ratio of GO, which is 1.02. The average C/O ratio of rGO increased to 4.378 after reduction from GO to rGO using AA assisted by magnetic stirring. The rGO structure contains fewer oxygen groups than GO. Furthermore, the increase in the C/O ratio for rGO compared to GO suggests that ascorbic acid with a concentration of 30% and a magnetic stirring duration of 50 minutes effectively removes oxygen from the GO surface.

Density Value Test

The density of solids is measured according to established standards for determining the specific gravity and density of semi-solid bituminous materials, asphalt cement, and soft tar pitch using a pycnometer (ASTM International, 2010). The formula used is as follows:

$$\frac{W2 - W1}{((W4 - W1) - (W3 - W2))}$$

where:

- W1 : weight of empty pycnometer
- W2 : weight of pycnometer + solids
- W3 : weight of pycnometer + solids + water
- W4 : weight of pycnometer + water

The density calculations for graphene oxide (GO) and reduced graphene oxide (rGO) are presented in **Table 6**. The density values of GO and rGO were calculated to be 1.1 g/cm³ and 1.45 g/cm³, respectively. These values are consistent with the theoretical density values of 0.98 g/cm³ for GO and 1.5-1.9 g/cm³ for rGO, as reported by (Torrissi et al., 2022).

Table 6. Calculation Results of GO and rGO Density

Sample	Density (g/cm ³)
GO	1,1
rGO	1,45

Solubility Test

Solubility tests on GO and rGO were conducted using three solvents: water, N-hexane, and toluene. **Figure 5** shows that GO is partially soluble in water solvents due to the presence of carbonyl and carboxyl groups, which make it hydrophilic. In contrast, rGO is hydrophobic and does not dissolve in water solvents. Additionally, GO is insoluble in n-hexane and toluene solvents, while rGO is partially soluble (Konios et al., 2014). Graphene oxide is challenging to dissolve in organic solvents due to the strong hydrogen bonds between neighboring layers, causing them to stick and interact strongly with each other.

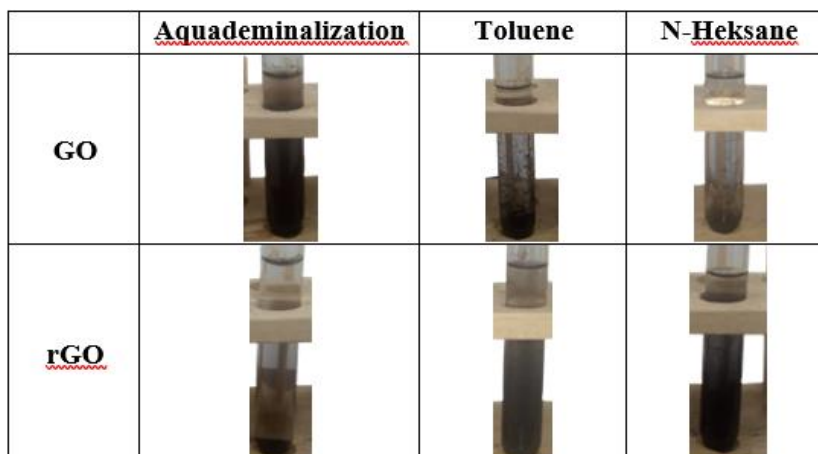


Figure 5. Solubility test of GO and rGO



CONCLUSIONS

This study synthesized reduced graphene oxide (rGO) from graphene oxide (GO) using ascorbic acid (AA) with variations in concentration and magnetic stirrer assistance based on variations in the length of stirring time. The results indicate that the optimal rGO was produced from GO using AA as a reducing agent with a concentration of 10% assisted by magnetic stirring for 50 minutes. The FTIR results indicate a decrease in oxygen groups in GO. This is supported by the SEM-EDX results, which demonstrate a change in morphology in GO after being reduced to rGO. EDX shows an increase in the C/O ratio in rGO compared to GO. Other tests, such as density, solubility, and pH, also confirm the feasibility of the reduction study of reduced graphene oxide (rGO) from graphene oxide (GO) using ascorbic acid (AA) with the help of a magnetic stirrer.

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REFERENCES

1. Andrijanto, E., Shoelarta, S., Subiyanto, G., & Rifki, S. (2016). *Facile Synthesis of Graphene from Graphite Using Ascorbic Acid as Reducing Agent*. 020003.
2. ASTM International. (2010). *Test Method for Density of Semi-Solid Bituminous Materials (Pycnometer Method)*. ASTM International.
3. Bakatula, E. N., Richard, D., Neculita, C. M., & Zagury, G. J. (2018). Determination of Point of Zero Charge of Natural Organic Materials. *Environmental Science and Pollution Research*, 25(8), 7823–7833.
4. Bychko, I., Abakumov, A., Didenko, O., Chen, M., Tang, J., & Strizhak, P. (2022). Differences in the Structure and Functionalities of Graphene Oxide and Reduced Graphene Oxide Obtained from Graphite with Various Degrees of Graphitization. *Journal of Physics and Chemistry of Solids*, 164, 110614.
5. Chua, C. K., & Pumera, M. (2016). The Reduction of Graphene Oxide with Hydrazine: Elucidating Its Reductive Capability Based on A Reaction-Model Approach. *Chemical Communications*, 52(1), 72–75.
6. Dai, L., Chang, D. W., Baek, J.-B., & Lu, W. (2012). Carbon Nanomaterials for Advanced Energy Conversion and Storage. *Small*, 8(8), 1130–1166.
7. Delmifiana, B. (2013). *Pengaruh Sonikasi terhadap Struktur dan Morfologi Nanopartikel Magnetik yang Disintesis dengan Metode Kopresipitasi*. 2(3).
8. Emiru, T. F., & Ayele, D. W. (2017). Controlled Synthesis, Characterization and Reduction of Graphene Oxide: A Convenient Method for Large Scale Production. *Egyptian Journal of Basic and Applied Sciences*, 4(1), 74–79.
9. Fernández-Merino, M. J., Guardia, L., Paredes, J. I., Villar-Rodil, S., Solís-Fernández, P., Martínez-Alonso, A., & Tascón, J. M. D. (2010). Vitamin C Is an Ideal Substitute for Hydrazine in the Reduction of Graphene Oxide Suspensions. *The Journal of Physical Chemistry C*, 114(14), 6426–6432.
10. Gao, J., Liu, F., Liu, Y., Ma, N., Wang, Z., & Zhang, X. (2010). Environment-Friendly Method To Produce Graphene That Employs Vitamin C and Amino Acid. *Chemistry of Materials*, 22(7), 2213–2218.
11. Go, S.-H., Kim, H., Yu, J., You, N.-H., Ku, B.-C., & Kim, Y.-K. (2018). Synergistic Effect of UV and L-Ascorbic Acid on the Reduction of Graphene Oxide: Reduction Kinetics and Quantum Chemical Simulations. *Solid State Sciences*, 84, 120–125.
12. Hsieh, C.-T., Lin, C.-Y., Chen, Y.-F., Lin, J.-S., & Teng, H. (2013). Silver Nanorods Attached to Graphene Sheets as Anode Materials for Lithium-Ion Batteries. *Carbon*, 62, 109–116.
13. Huda, M., Salinita, S., & Ningrum, N. S. (2017). Perubahan Komposisi Maseral dalam Batubara Wahau Setelah Proses Pengeringan/Upgrading. *Jurnal Teknologi Mineral Dan Batubara*, 13(3), 225.
14. Jakhar, R., Yap, J. E., & Joshi, R. (2020). Microwave Reduction of Graphene Oxide. *Carbon*, 170, 277–293.
15. Konios, D., Stylianakis, M. M., Stratakis, E., & Kymakis, E. (2014). Dispersion Behaviour of Graphene Oxide and Reduced Graphene Oxide. *Journal of Colloid and Interface Science*, 430, 108–112.



16. Longo, A., Verucchi, R., Aversa, L., Tatti, R., Ambrosio, A., Orabona, E., Coscia, U., Carotenuto, G., & Maddalena, P. (2017). Graphene Oxide Prepared by Graphene Nanoplatelets and Reduced by Laser Treatment. *Nanotechnology*, 28(22), 224002.
17. Mutrofin, S., Wardhani, S., & Misbah Khunur, M. (2021). *Preparasi Nanopartikel Batubara Loa Janan Kalimantan Timur Hasil Pencucian dengan Teknik Sonikasi [DPP/SPP]*. Universitas Brawijaya.
18. Nadia, L. M. H., Suptijah, P., & Ibrahim, B. (2014). Production and Characterization Chitosan Nano from Black Tiger Shrimp with Ionic Gelation Methods. *Jurnal Pengolahan Hasil Perikanan Indonesia*, 17(2).
19. Nandiyanto, A. B. D., Oktiani, R., & Ragadhita, R. (2019). How to Read and Interpret FTIR Spectroscopy of Organic Material. *Indonesian Journal of Science and Technology*, 4(1), 97.
20. Palomba, M., Carotenuto, G., & Longo, A. (2022). A Brief Review: The Use of L-Ascorbic Acid as a Green Reducing Agent of Graphene Oxide. *Materials*, 15(18), 6456.
21. Pei, S., & Cheng, H.-M. (2012). The Reduction of Graphene Oxide. *Carbon*, 50(9), 3210–3228.
22. Pratomo, Moh. D., Wardanidan, D. W., Revonagara, N. A., Ersyah, D., Setijawati, D., Yufidasari, H. S., & Jaziri, A. A. (2020). Karakteristik Pepton dari Limbah Ikan Kurisi (*Nemipterus* sp.) sebagai Media Pertumbuhan Bakteri yang Terjamin Halal. *Journal of Aquaculture and Fish Health*, 9(2), 104.
23. Rowley-Neale, S. J., Randviir, E. P., Abo Dena, A. S., & Banks, C. E. (2018). An Overview of Recent Applications of Reduced Graphene Oxide as a Basis of Electroanalytical Sensing Platforms. *Applied Materials Today*, 10, 218–226.
24. Santoso, A. D. (2018). Keragaan Nilai DO, BOD dan COD di Danau Bekas Tambang Batubara Studi Kasus pada Danau Sangatta North PT. KPC di Kalimantan Timur. *Jurnal Teknologi Lingkungan*, 19(1), 89.
25. Taurina, W., Sari, R., Hafinur, U. C., Wahdaningsih, S., & Isnindar, I. (2017). Optimization of Stirring Speed Time Toward Nanoparticle Size of Chitosan-Siam Citrus Peel (*Citrus nobilis* L. var *Microcarpa*) 70% Ethanol Extract. *Majalah Obat Tradisional*, 22(1), 16.
26. Torrisi, L., Cutroneo, M., Torrisi, A., & Silipigni, L. (2022). Measurements on Five Characterizing Properties of Graphene Oxide and Reduced Graphene Oxide Foils. *Physica Status Solidi (a)*, 219(6), 2100628.
27. Utkan, G., Öztürk, T., Duygulu, Ö., Tahtasakal, E., & Denizci, A. A. (2019). *Microbial Reduction of Graphene Oxide by Lactobacillus Plantarum*.
28. Wijayanto, S. O., & Bayuseno, A. P. (2014). *Analisis Kegagalan Material Pipa Ferrule Nickel Alloy N06025 pada Waste Water Heat Boiler Akibat Suhu Tinggi Berdasarkan Pengujian: Mikrografi dan Kekerasan*. 2(1).
29. Yan, Y., Nashath, F. Z., Chen, S., Manickam, S., Lim, S. S., Zhao, H., Lester, E., Wu, T., & Pang, C. H. (2020). Synthesis of Graphene: Potential Carbon Precursors and Approaches. *Nanotechnology Reviews*, 9(1), 1284–1314.
30. Yustanti, E. (2012). *Pencampuran Batubara Coking dengan Batubara Lignite Hasil Karbonisasi sebagai Bahan Pembuatan Kokas*. 15.
31. Zhu, Q. (2014). *Coal Sampling and Analysis Standards*. IEA Clean Coal Centre.

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