The Effect of Stirring Time and Citric Acid Concentration on the Yield of Reduce Graphene Oxide (r-GO) from Loa Janan Bituminous Coal East Kalimantan

Fadilah Alifiyah Maharani and Siti Mutrofin[*]

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Brawijaya University, Indonesia
[*]Corresponding Author: mutrofin@ub.ac.id

Abstract: *Loa Janan bituminous has a carbon content of 70,64%. It is a good candidate to isolate graphene oxide (GO) and convert it to reduce- graphene oxide (r-GO). Usually, the Staudeinmeir and Hummers method are applied to produce GO, but in this research the GO was produced using sonication under pH 4. Then the GO was converted to r-GO using citric acid (10%, 30%, 50%) and the reaction was accelerated using magnetic stirrer for the duration of 10, 30, 50 minutes. The best r-GO was chosen based on the lowest yield of it. It was gained at 10% of citric acid and 10 minutes contact time of stirring (95.70%). Fourier transform infra red characterization resulted of prominent peaks of trasmitance percentage for C-OH (68.12%), C-O-C (100%) and C=C (78,79%). According to scanning electron microscopy (SEM), there was no different between its morphology with references. The ratio C:O of selected r-GO was 4.35 and the one for GO was 1.92 calculated from energy dispersive X-ray data . It is density and pH value were 1.39 g/cm^3 (r-GO) and 1.12 g/cm^3 (GO).*
Keywords: *reduced-graphene oxide, stirring, citric acid, bituminous coal*

I. INTRODUCTION

Coal was a sedimentary rock produced by living organisms that is classified in the sedimentary hydrocarbon group which has flammable properties. This is because coal is partly composed of carbon and is formed from plant remains through a coalification process that lasts for millions of years. Coalification is the process by which peat turns into coal and occurs in two steps, namely biochemical and physicochemical stages. In the biochemical process, organisms turn peat into brown coal (Voncken, 2020). Coal is one of the fossil energy sources. Coal undergoes several changes during the formation phase. Coal is formed in swampy areas due to the decay of plants in the absence of oxygen. When plants in swamp forests die, they sink underwater and begin the process of coal formation. Coal is classified into lignin, subbituminous, bituminous and anthracite. This classification is based on the quality of its use. Generally, coal with high ash and sulfur content is considered as coal with low quality (Huda et al., 2017). In coal there are external and internal impurities. External impurities in the form of soil attached to the coal surface. Meanwhile internal impurities are SiO_2, Al_2O_3, $CaSO_4$, $Al_2Si_2O_5(OH)_4$, $FeCO_3$, Fe_2O_3, FeS_2 and other metal oxides. Silica content is uasually the highet amount of coal chemical composition followed by alumina, sulfur oxides and other oxide elements. While Loa Jonan coal, silica content is in the second position after iron (Fe oxide). The iron content in Loa Janan coal reaches 2 (two) times amount compored to silica (Mutrofin et al., 2021). Coal is generally utilized directly to produce heat which is used as process energy in industry and energy for electrical power generation. Coal can be converted as fuel gas, liquid fuel or activated carbon. Low-ranked coal is dried before use and converted to reduce moisture content and increase heating value. High-ranked coal has a lower moisture content and the conversion process requires a reactor (Huda, et al., 2017). Coal is also one of the sources of natural graphite which can have a graphitization degree of >80% (Chen et al., 2013). Therefore, coal can be a source/material in the manufacture of r-GO (reduced graphene oxide).

Graphene is one of the forms of carbon that has a certain structure. Graphene has a two-dimensional system with one atomic plane arranged in a hexagonal lattice and shaped like a honeycomb. Graphene is a layer of mono atoms obtained from isolated graphite (Johannes, 2018). Graphene is a two-dimensional form of carbon and has superior electronic properties. The electronic properties of graphene include high charge carrier mobility to more than 200,000 cm^2 /Vs. Another property of graphene besides having high conductivity, graphene is the strongest material in the world. Graphene has a tensile strength of 1Tpa. Thus, graphene is a material that is a new challenge for the development of the electronics industry, aircraft and the automotive industry (Azizah & Susanti, 2014). Graphene can also be applied in various fields, especially in the energy sector (Thebora et al., 2019). Graphene is part of a nanomaterial that can be synthesized from a practical carbon source, namely coal

(Vivi Purwandari et al*.,* 2021). There is graphene oxide which is the easiest derivative of graphene to be synthesized. Graphene oxide has oxygen functional groups found on the base plane and sheet edges. The properties of graphene oxide are influenced by its unique chemical structure and consist of small sp^2 carbon domains surrounded by sp^3 carbon domains and oxygen containing hydrophilic functional groups (Sjahriza & Herlambang, 2021). Graphene oxide is chemically modified graphene, containing oxygen-carrying functional groups that can reduce its thermal stability. The characteristics of graphene oxide are an important reference to obtain graphene whose properties can be suitable for certain applications with lower or higher conductivity compared to pure graphene (Sari et al., 2022). Graphene oxide is the result of oxidation of graphite with the addition of oxygen and some Van der Waals bonds are broken, so that the thickness of the material is reduced. Another derivative of graphene is r-GO (reduced graphene oxide). r-GO is the result of oxygen reduction from GO, which removes functional groups, to increase electrical conductivity. The properties of r-GO resemble the properties of graphene, but r-GO has defects caused by the presence of oxides inserted in its structure (Safitri & Kusuma, 2020).

There are several attempts to isolate or synthesize graphene oxide from graphite, namely: Brodie method, Staudenmaier method, and Hummers method. The Brodie method is a method of synthesizing graphene oxide by adding $KClO_3$ to graphite and reacting in HNO_3 under fumigation at 60 ^oC for 4 days. The Staudenmaier method is an improvement of the Brodie method. In this method, 2/3 of the HNO_3 fumigation is replaced by using concentrated H_2SO_4 and the addition of $KClO_3$. The reaction in this method occurs for 4 days. The Staudenmair method is a graphite oxidation method using coarse treatment, where graphite is dissolved in $KMnO_4$ and $NaNO_3$ is added (Chen et al., 2013). However, these three methods have disadvantages, namely: time consuming, using hazardous chemicals, producing harmful gases such as NO_2 and N_2O_4, and producing Na^+ ions and NO_3^- ions that are difficult to remove from wastewater (Chen et al., 2013). The latest method that can convert graphite from coal into graphene oxide is by sonication for 3 hours with the addition of 0.1 M HCl to set at pH 4 (Mutrofin et al., 2021). The research is the latest research that is more environmentally friendly and shorter the reaction route compared to previous methods and does not produce hazardous waste and follows the principles of Green Chemistry.

The synthesis of r-GO from GO can be done by using organic acids as reductant agents (Andrijanto et al., 2016). Citric acid is a weak organic acid found in the leaves and fruits of plants in the citrus genus (oranges). Citric acid is found in various types of fruits and vegetables, but is found in high concentrations, reaching 8% dry weight in lemons and limes (Indah Purwaningsih & Kuswiyanto, 2016). Citric acid is a compound that can reduce metals oxidation number and can take free radicals in a solution. Citric acid has a functional group (OH and COOH) so that it can reduce or oxidize in the presence of high H^+ concentrations at low pH conditions (Srwar et al., 2021). In the process of making r-GO from coal, the use of citric acid as a reductant will remove and reduce mineral matter and metal ions and the amount of oxygen so that the organic structure of GO becomes a heterogeneous aromatic structure (Manoj & Narayanan, 2013). The method used to obtain r-GO is the stirring method. Stirring is one of the mechanical methods which can also be called a destructive method that causes large molecules to break down into smaller size and then turns into nanoparticles (Ijaz et al., 2020). The application of mechanical methods to separate layered materials by stirring is one of the most effective ways in the process of cutting graphene layer (Islamiyah, 2017). Increasing the speed and length of time of stirring will cause a decrease in the size of the particles. This is because, with the speed accompanied by a long stirring will cause a particle to split and even convert to nano-sized compound. The higher the rotation speed of the stirring will increase the intensity of solvent molecules and particles colliding with each other which will cause the resulting particles to be smaller (Taurina et al., 2017). Stirring that is too high can cause deformation of a substance into another form of substance and possibly change the morphology of the surface of the synthesized or isolated substance (Rahayu et al., 2018). This is because stirring can cause the breakage of bonds in a molecule. In the case of r-GO synthesis from GO, the stirring method is expected to break the bonds between carbon and attached groups, especially those containing oxygen.

Based on the theoretical background, this research aims to analyze the effect of citric acid concentration as a reductant and the length of time for stirring on the yield of r-GO (reduced graphene oxide) from GO (graphene oxide) derived from Loa Janan Bituminous coal in order to obtain the best yield percentage of r-GO.

II. EXPERIMENTAL PROCEDURE

2.1 Preparation of Coal Sample

Bituminous Loa Janan coal obtained from Augerah Bara East Kalimantan company was pulverized by pounding using a porcelain grinder and mortar. The pulverized coal was sieved using 150 and 200 mesh sievers. The separated coal that passes the 150 mesh siever and is retained on the 200 mesh siever is used for futher treatment. This coal is labelled as 150-200 mesh coal sample or 74,000 nanometers (74 μm). The sieved coal was placed in a porcelain cup and covered to be heated in an oven for 10 hours at 40 ^oC. After 10 hours of

heating, the coal was placed in a desiccator for the cooling stage. Then, the coal sample was washed with aquadest in ratio of 1:5 using a magnetic stirrer for 3 hours at room temperature with a speed scale of 6-7 (1500 rpm). The washed coal will be filtered using hawach filter paper with a pore size of 11 μm placed in a glass funnel. The filtrate will be collected in an erlenmeyer. The filtered coal was transferred into a porcelain cup and covered with a cup cover or aluminium foil. Then, heated in an oven at 40 $^{\circ}$C for another 10 hours. At last, the coal was placed in a desiccator until it cools down and put in a bottle or sample container.

2.2 Isolation of GO (Graphene Oxide) from Coal

This procedure was accordance to the research conducted by Mutrofin et al (2021). A total of 5 grams of coal that has been prepared was weighed with an analytical balance and put into a 500 mL erlenmeyer. It was about 250 mL of aquadest added. The pH was checked with pH indicator paper and recorded as the initial pH. Then conditioning the pH of the coal sample solution at pH 4 using 0.1 M HCl. The coal sample solution that already had a pH of 4 was transferred into a 500 mL erlenmeyer. Then sonicated for 3 hours with an interval of 1 hour and a break of 30 minutes. Then, the solution was filtered using hawach filter paper with a pore size of 11 μm placed in a glass funnel. The filtrate obtained will be collected in erlenmeyer. The filtered sediment on the filter paper was placed on a porcelain cup to be heated in an oven for 10 hours at 40 $^{\circ}$C. The heating product was placed in a desiccator and transferred to a labeled sample bottle.

2.3. Isolation of r-GO (reduced graphene oxide) with Various Citric Acid Concentration

A total of 1 gram of graphene oxide that has been produced from **2.2**, is weighed with an analytical balance and put into a 100 mL beaker glass. It was about 50 mL of aquadest added. Then stirred with a magnetic stirrer for 2 hours. Added variations concentraton of citric acid solution (10%, 30% and 50%) as a reductant in each solution and stirred for 30 minutes. Filtering was carried out using hawach filter paper with a pore size of 11 μm which was placed in a glass funnel. The filtrate obtained will be accommodated in an erlenmeyer. The filtered sediment on the filter paper was placed on a porcelain cup to be heated in an oven for 24 hours at 50 $^{\circ}$C. The heating results were placed in a desiccator and transferred to a labeled sample bottle and it was ready to be characterized. The procedure was run in duplicate form. The selected r-GO was the one which has the lowet yield (with the assumption it has the lowest impurities).

2.4. Isolation of r-GO (reduced graphene oxide) with Various Stirring Time

A total of 1 gram of graphene oxide that has been produced from **2.2**., is weighed with an analytical balance and put into a 100 mL beaker glass. It was about 50 mL of aquadest added. Then stirred with a magnetic stirrer for 2 hours. The optimum concentration of citric acid was added as a reducing agent based on the previous procedure (**2.3**.). Stirred with variations in the length of time of 10, 30 and 50 minutes in each solution..Filtering was carried out using hawach filter paper with a pore size of 11 μm, which was placed in a glass funnel. The filtrate obtained was collected in an erlenmeyer. The filtered sediment on the filter paper was placed on a porcelain cup to be heated in an oven for 24 hours at 50 $^{\circ}$C. The heating results were placed in a desiccator and transferred to a labeled sample bottle and it was ready to be characterized. The procedure was run in duplicate form. The selected r-GO was the one which has the lowet yield (with the assumption it has the lowest impurities).

2.5. Characterization Techniques

The selected r-GO yield based on the **2.4**. procedure was characterized using a 1 mL pycnometer Variation fts 1000 and SEM-EDX thermo scientific Phenom Prox. The pycnometer is used to measure the density or specific gravity of the isolated r-GO. Fourier transform infrared (FTIR) was used to characterize the functional groups on GO and r-GO. While Scanning Electron Microscope (SEM) & Energy Despersive X-ray (EDX) was used to obtain information in the form of shape, morphology, and composition of both elements and oxides of GO and r-GO. The pH test was also carried out on the filtrate from the filtration process of isolation of GO and r-GO using a pH indicator. In addition, a piece of GO and r-GO yield was tested for solubility in 10 mL of n-hexane, toluene, and aquadest.

III. RESULTS AND DISCUSSION

3.1 Preparation of Coal Samples

Coal sample preparation was based on the research of Mutrofin et al (2021) [4]. The purpose of refinement coal samples is to reduce the size of Loa Janan coal to a size of 150-200 mesh or equivalent to 74,000 nm (74 μm). It will increase the surface area and increase the active side of the coal so that it allows coal to optimally contact with other substances (Prinandito et al., 2018). Heated using oven for 10 hours at 40 $^{\circ}$C on coal aim to evaporate volatile organic compounds in the coal. Washed of coal samples aims to remove and minimize the presence of impurities in coal samples. The coal was washed using aquadest, so that it is expected

that impurities in coal will be dissolved/hydrated/solvated/complexed. There is a difference in content/composition between untreated coal and treated coal. Loa Janan coal after treatment has an increased C element content, but the content of other elements such as O decreases (Mutrofin et al., 2021).

3.2 Isolation of GO (Graphene Oxide) from Coal

This procedure involved the addition of 0.1 M HCl and sonication for 3 hours. HCl is a strong acidic compound that acts as an oxidizing agent. H^+ from HCl will bind to metal oxides to form solvated/hydrated metal oxides. Meanwhile, Cl^- will bind to the cationic elements in the coal. The sonication method is a method that uses sound energy to agitate a particle in the sample. This method had the principle of breaking intermolecular reactions in the sample so that nano-sized particles can be produced (Nandiyanto et al., 2019). The addition of 0.1 M HCl accompanied by the use of sonication in this process had several advantages, that is: inexpensive, simple, less time-consuming, sorter the reaction route, does not use chemicals with high concentrations and minimizes hazardous waste. The filtrate from the GO isolation process obtained pH 5 with the color of the solution is clear. This indicates that impurities both in the form of oxide groups and in the form of elements present in the prepared coal successfully oxidize with HCl and produce H_2O and carboxyl groups due to the breaking of hydrogen bonds. In addition, the filtered GO was heated for 10 hours at 40 °C to evaporate volatile organic compounds in the coal. The purpose of heated allow the water to evaporate slowly.

3.3 Isolation of r-GO (reduced graphene oxide) with Various Citric Acid Concentrations

In this procedure, citric acid variations of 10, 30, and 50% were used. Citric acid was one of several organic acids (Puspadewi et al., 2017). Citric acid can be used as a reducing agent in the production of nanoparticles by simple chemical methods. The use of citric acid as a reductant was based on its natural, environmentally friendly nature, can reduce the impact of harmful chemical pollution, and abundant availability. (Yashashri et al., 2017). In the process of isolated r-GO from coal, the use of citric acid will remove impurities of mineral matter and metal ions that still remain in GO as a citrate complex and form carbocations and H_2O. In addition, citric acid as an organic acid will reduce the oxygen-containing functional groups on GO (Andrijanto et al., 2016). The filtrate from the r-GO isolation process obtained pH 2 with the color of the solution was yellowish This may indicate that citric acid had reduced the impurity compounds and the amount of oxygen on GO to form a clear yellowish filtrate. The change in color of citric acid from clear to yellowish indicates that citric acid was react with impurities and oxygen-containing groups on GO to form a complex and H_2O. The lowest yield in this process is the optimum yield. This is based on the hypothesis that at low yields, impurities and oxide groups on GO have been lost and reduced, so the weight (grams) of r-GO produced will decrease. The weight was equivalent to the molecular weight. Thus, the optimal yield of r-GO was in the 10% citric acid concentration. The yield of r-GO in the variation of citric acid concentration of 30% and 50% had a % yield of more than 100%, as tabulated in **Table 1**. It is possible that the addition of excess citric acid may cause alternating reactions that trap citric acid on the GO. In this case, citric acid, which originally acted as a reducing agent, becomes an impurity that binds strongly to GO. This can cause an increase in weight.

Table 1. Yield of r-GO with Various Citric Acid Concentration

Yield of r-GO with Various Citric Acid Concentration (%)			
Repetition	**10%**	**30%**	**50%**
1	95.76	106.96	115.45
2	97.80	106.60	113.02
Average	96.78	106.78	114.24

3.4 Isolation of r-GO (reduced graphene oxide) with Various Stirring Time

In this process, citric acid was added at the optimal concentration in the previous process, which was 10%, and then a variation of stirring time of 10, 30 and 50 minutes was performed as shown in **Table 2**. The stirring method was included in the top-down method, which was a simple and environmentally friendly route, but involves a long grinding time (Voncken, 2020). An example of a simple agitation method was the use of a magnetic stirrer. A magnetic stirrer was a device that creates a magnetic field with circular motion and consists of a plastic-coated magnetic bar. It is possible to create circular motion due to the rotating magnetic field (Yashashri et al., 2017). The greater the intensity of the rotational speed used in the magnetic stirrer, the more solvent molecules will come into contact with the particles, resulting in smaller particles (Taurina et al., 2017). In this process, the added citric acid contacted and reacted with the GO by stirring. The citric acid will bind to mineral impurities and metal ions as well as oxygenated functional groups on GO. With stirring, all these impurities were released from the GO as citrate complexes, forming carbocations and H_2O. The stirring speed used in this process is 6-7 scale (1500 rpm), which was a high speed scale. It can cause deformation of a substance into another form of substance and possibly change the morphology of the surface of the synthesized or isolated substance (Rahayu et al., 2018). This is because stirrer can cause the breaking of chemical bonds in a

compound. The results of the % yield from variations in stirring time were statistically tested using the T-test. The results of the third T-test of the % Yield for each variation of stirring time indicated that there was no significant difference in the overall sample. Thus, the selection of yield was based on time efficiency, namely the variation of 10 minutes stirring time.

**Table 2**. Yield of r-GO with Various Stirring Time

Yield of r-GO with Various Stirring Time (%)			
Repetition	10 minutes	30 minutes	50 minutes
1	94.76	95.76	95.78
2	96.64	97.80	98.63
Average	95.70	96.78	97.205

3.5 Characterization

3.5.1 Fourier transform infrared (FTIR)

Fourier transform infrared (FTIR) characterization was performed to determine the functional groups contained in the GO and R-GO that were previously isolated, it can bee seen in **Figure 1**. The wavelength used in this study is between 4000 cm^{-1}-400 cm^{-1}

Figure 1. The Infraed Spectra of (a) GO and (b) r-GO at Various Stirring Time
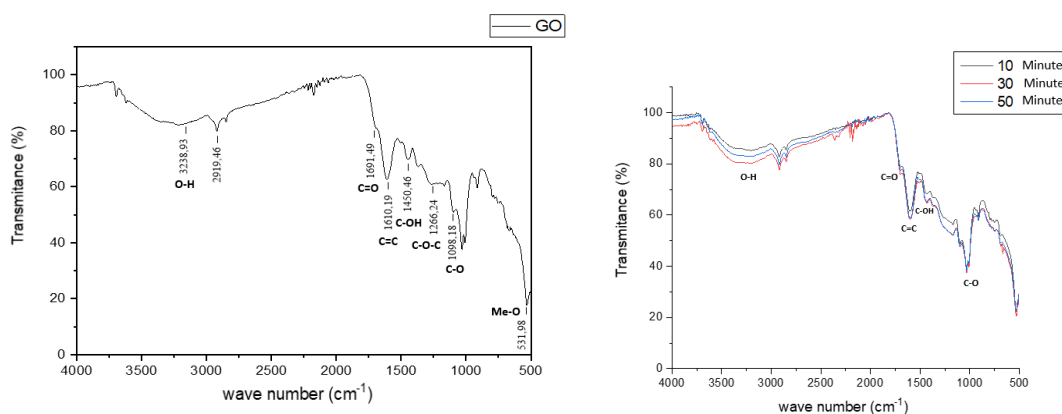
Graphena Oxide has a hexagonal carbon structure similar to graphene, but contains hydroxyl (-OH), alkoxy (C-O-C), carbonyl (C-O), carboxylic acid (-COOH) and other oxygen-based functional groups (Smith et al., 2019). Graphena Oxide had a strong and broad peak at 3410 cm^{-1} showing O-H stretching, a peak at 1721 cm^{-1} showing C=O carboxyl stretching, a peak at 1404 cm^{-1} showing vibrations due to O-H deformation, and a peak at 1087 cm^{-1} showing C-O stretching (Ciplak et al, 2015). Infrared analysis of GO shows a peak at 1066 cm^{-1} caused by C-O stretching vibrations, a peak at 1288 cm^{-1} caused by C-O-C bending, a peak at 1587 cm^{-1} caused by bending of C-OH group. There is a peak indicating a carbonyl group at 1724 cm^{-1} caused by C=O stretching and a broad peak at 3448 cm^{-1} caused by O-H (Andrijanto et al., 2016). Thus, the infrared results of GO isolated in this study were in accordance with previous researchers. It can be seen in the figure that the broad peak at 3238.93 cm^{-1} , which shows the stretching vibration of -OH, the peak at 1691.48 cm^{-1} is for the C=O carbonyl group, the peak at 1610.19 cm^{-1} is for the C=C, the peak at 1450 cm^{-1} is for the C-OH group, the peak at 1266.24 cm^{-1} is the bending of C-O-C, and there is a peak at 1098.18 cm^{-1} is for the stretching vibration of C-O. The functional groups contained in r-GO are C=C, C-O, C=O and OH bonds. The main functional groups possessed by GO and r-GO are C=C and OH functional groups. Both spectra of GO and r-GO is in **Figure 2 and Table 3**. The two functional groups bond together to form a hexagonal structure of carbon atoms. The C = C functional group becomes the basic structure of GO and r-GO, which binds together and forms a hexagonal (Kristiyanti & Dwandaru, 2021). As the absorbance increases, the intensity of the absorbed light is greater, indicating an increase in the concentration/content of compounds. The higher the absorbance value means the lower the transmittance value. The absorbance (A) is inversely proportional to the transmittance (T) and directly proportional to the content of a compound (Fauzi & Dwandaru, 2021). The reduced graphene oxide (r-GO) stirring time variation of 10 minutes has a highe transmittance percentage than the stirring time variation of 30 and 50 minutes, especially at wave numbers 3600-3300 cm^{-1} showing -OH group, wave number 1700 cm^{-1} showing C=O group, and wave number 1000 cm^{-1} showing C-O group. This states that in the isolation of r-GO, the variation of stirring time of 10 minutes can reduce oxygen-containing functional groups better than other variations

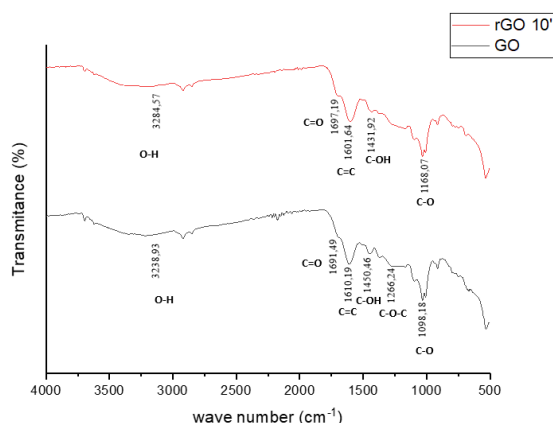**Figure 2.** Infrared Spectra of Selected r-GO and GO

Table 3. %Tranmittance of r-GO 10' and GO

Wave Number (cm-1)	functional group	%Transmittance	
		GO	r-GO 10'
3700-3584	O-H	92.35	95.85
3550-3300	O-H	-	-
3000-2840	C-H	79.87	82.70
1670-1600	C=C aromatic	62.56	78.79
1400	C-OH	69.75	68.12
1200-1100	C-O-C	60.84	-
600-400	Me-O	13.68	10.00

Based on the **Figure 2** and **Table 3**, the r-GO peak shows the reduction of oxygen-containing groups on GO by citric acid. This can be seen from the transmittance percentage, which shows the reduction and removal of the peak intensity. In **Figure 2**, the removal of the C-O-C group on r-GO is indicated by the absence of a peak at 1266.24 cm^{-1}, which was previously detected on GO. Meanwhile, there was an increase in transmittance percentage on r-GO with a stirring time of 10 minutes. The increase in % T was clearly visible at wave numbers 3600-3200 cm^{-1}, indicating the -OH group. Thus, citric acid was able to reduce the OH group on GO. The results of the FTIR characterization of this study were consistent with the previous one, which states that the synthesis of r-GO was not completely reduced because it still contains some oxide groups, and r-GO was completely reduced when it contains no oxide groups and the resulting functional group is only C=C (Kristiyanti & Dwandaru, 2021). The possible reaction citric acid with GO is in **Figure 3**.

Figure 3. Reaction GO with citric acid
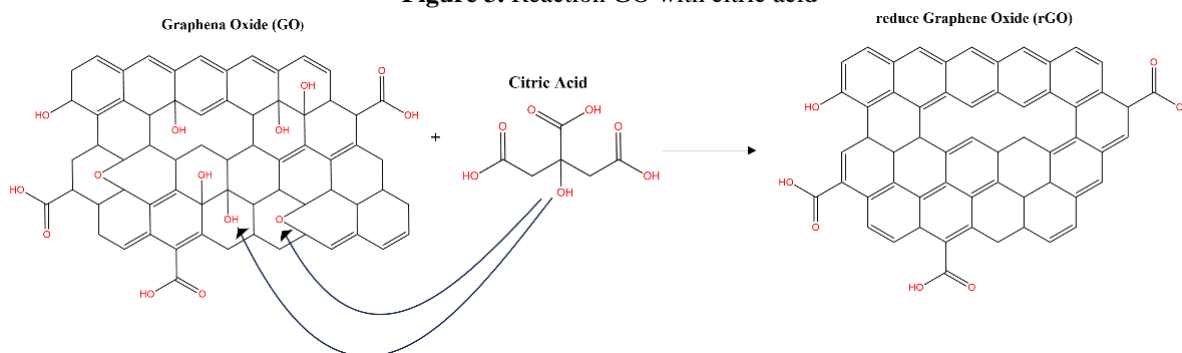
3.5.2 Density Test

Density testing of GO and r-GO used a 1 mL pycnometer was performed according to ASTM D70-03 procedures. Used the following formula:

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

W1 = The weight of the empty pycnometer
W2 = The weight of the pycnometer and solids
W3 = The weight of the pycnometer, water and solids.
W4 = The weight of the pycnometer and water.

Based on this formula, the density of GO was 1.12 g/cm^3 while r-GO had a density of 1.39 g/cm^3. Each of these densities is close to the theoretical density. The theoretical density of GO is 0.981 g/cm^3, while the theoretical density of r-GO is 1.5-1.9 g/cm^3 (Torrisi et al., 2022). There are factors that can affect the difference in density values of research results with theoretical, one of which is stirring. The stirring method used in this study is a scale of 6-7 or equivalent to 1500 rpm, which is a high-speed scale. It can cause the break of chemical bonds in a compound (Rahayu et al., 2018). The chemical bonds that are broken can reduce the density and molecular weight of the isolated r-GO yield, so the density calculation may differ from the theory.

3.5.3   Solubility Test

Solubility test was conducted to see the solubility of GO and r-GO in 3 solvents, namely: n-hexane, toluene and aquadest, is in **Table 4**. Graphene oxide cannot dissolve in organic solvents n-hexane and toluene, which were non-polar. This is because GO had an -OH group, so it was polar and easily soluble in aquadest, which also had an -OH group. Recuded grapphen oxide (r-GO) was defective graphene because it still has an OH group, but most of the OH groups of r-GO have been reduced by citric acid, so the properties and solubility of r-GO are the same as /similar to graphene. Graphene cannot dissolve in water because it had no -OH group. This was on accordance with the statement that graphene oxide has hydrophilic properties that like water, so it dissolves easily in water to form a brown solution, while graphene has hydrophobic properties that are difficult to dissolve in water (Konios et al, 2014).

Table 4. Solubility Test Results

	n-Hexane	Toluene	aquademineralization
GO	insoluble	insoluble	Soluble
r-GO	partially dissolved	partially dissolved	insoluble

3.5.4   Scanning Electron Microscopy (SEM) & Energy Dispersive X-ray (EDX)

Scanning Electron Microscopy analysis was used to understand the surface of GO and r-GO materials, while energy dispersive X-ray (EDX) analysis was used to determine the carbon and oxygen content in GO and r-GO. The sem images are in **Figure 5**. The results of surface morphology analysis of GO are different from those of r-GO. The ratio of carbon atoms to oxygen of GO was smaller than that of r-GO (Fauzi & Dwandaru, 2021).

Figure 4. Morfology of GO (a-b), r-GO (c-d) at 10,000x Magnification
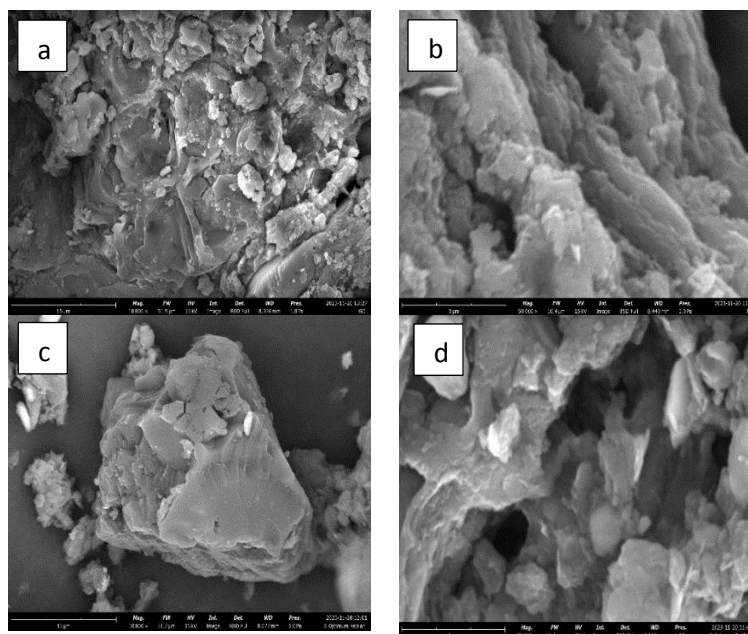
Scanning Electron Microscope results on GO show that the morphology of GO was in the form of flake sheets that were irregularly layered, but the gap between layers can be seen. The morphology of GO looks very thick, which was due to the presence of oxygen functional groups bound in it. While the morphology of r-GO shows that r-GO was thinner than GO. In addition, the morphology of r-GO shows thin layers with decreasing interlayer distance. There are similarities between the SEM results of this research and the literature as well as

the morphology. After the graphite contained in coal is oxidized and sonicated, the morphology was in the form of layered sheets, so it looks thick and the distance between the layers was clearly visible. The thickness of the GO morphology was due to the presence of bound oxygen functional groups. This indicates that the graphite has been exfoliated during the oxidation process (Wahyuningsih et al., 2020). Meanwhile, the morphology of r-GO shows that r-GO had a thin sheet morphology compared to GO and the distance between the layers decreases. The morphology of GO is uneven and irregular flakes, while the morphology of r-GO shows flakes that accumulate due to the loss of oxygen groups on the GO surface, causing the distance between the layers to decrease (Pattarith & Areerob, 2020). Scanning Electron Microscope (SEM) analysis showed that the pore diameter of r-GO increased compared to GO. The pore diameter of r-GO is larger than that of GO. This was due to the loss of oxide groups due to the use of citric acid, which causes r-GO to have a larger pore diameter.

There are differences in the EDX results of GO and r-GO, the data can be seen in **Table 5** and **Table 6**. The elemental oxygen content of r-GO is lower than that of GO. This indicates that citric acid had successfully reduced the amount of oxygen in GO to form r-GO. The comparison of carbon and oxygen content expressed as C:O ratio at three different surface points of GO and r-GO. Based on the calculation of the C:O ratio of GO and r-GO in Table 5 and Table 6, it can be seen that the C:O ratio of GO was 1.9366 and r-GO was 4.35108. There was an increase in the C:O ratio from GO to r-GO. This shows that the use of citric acid as a reducing agent can reduce oxygen-containing groups, namely -OH, C=O, C-OH, and C-O-C groups on GO. Previous research indicates that organic acids, such as ascorbic acid, can increase the C:O ratio of GO by 1.60 to r-GO by 4.03 (Tran, 2020). Thus, it can be seen that the use of citric acid was effective in reducing the amount of oxygen in GO.

Table 5. Carbon Oksigen Ratio (C:O) of GO

% Atomic Carbon Oxygen Ratio of GO				
Elements	Spot 1	Spot 2	Spot 3	Average C:O
C	50.468	56.806	53.552	1.9366
O	34142	27.911	23.318	
C/O	1.4781	2.0352	2.2965	

Table 6. Carbon Oxygen Ratio (C:O) of r-GO

% Atomic Carbon Oxygen Ratio of r-GO				
Elements	Spot 1	Spot 2	Spot 3	Average C:O
C	75.953	76.391	75.201	4.35108
O	15.131	17.852	20.03	
C/O	5.0196	4.2791	3.7544	

IV. CONCLUSION

It can be concluded that the isolation of r-GO (Reduced Graphene Oxide) from GO (Graphene Oxide) derived from bituminous coal of East Kalimantan has been carried out. This is indicated by the results of density test of GO and r-GO, 1.12 g/cm^3 and 1.39 g/cm^3 respectively. The solubility test shows that GO is soluble in aquadest but insoluble in n-hexane and toluene. Meanwhile r-GO was insoluble in aquadest, but partially soluble in n-hexane and toluene. The filtrate of GO filtration shows pH 5 and r-GO shows pH 2 due to the presence of citric acid. The results of the FTIR spectra of GO and r-GO shows an increase in transmittance percentage on r-GO, which indicates that citric acid has succeeded in reducing oxygen-containing groups, namely -OH, C=O, C-OH and C-O-C groups. Scanning electron microscopy analysis showed that the isolated r-GO had larger pores compared to GO. The morfology of r-GO shows thinner layers compared to GO. Graphene Oxide morphology looks very thick, this is due to the presence of oxygen functional groups bound in it. According to the Energy dispersive X-ray analysis, there is an increased in the C:O ratio in GO which is 1.9366 and rGO which is 4.35108. Thus, it can be concluded that the isolation of rGO (reduced graphene oxide) from GO (graphene oxide) obtained from East Kalimantan bituminous coal has been successfully carried out.

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