SYNTHESIS AND CHARACTERIZATION OF RISE HUSK NANOPORES CARBON THROUGH ULTRASONIC IRRADIATION WITH H$_3$PO$_4$ ACTIVATORS AS ELECTROCHEMICAL ENERGY STORAGE MATERIALS

Sitti Rahmah$^{1,3*}$, Muhammad Zakir$^{1,3}$, Musa Ramang$^{2,3}$

$^1$Physical Chemistry Laboratory, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University
$^2$Analytical Laboratory, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University
$^3$Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University, Perintis Kemerdekaan Street KM 10, Tamalanrea Makassar, Indonesia 90245

*Corresponding author: rahmah.kf@gmail.com

Abstract. The research on synthesis and characterization of carbon nanopores rice husk through ultrasonic irradiation by activators H$_3$PO$_4$ as electrochemical energy storage material has been made. This activated carbon is a basic material in making electrodes which will be developed into electrochemical energy storage material. Nanopores carbon is made from rice husks, which passes through three stages of the process and the development methods of manufacturing of previous activated carbon. Carbonization carried out at a temperature of 350 °C, then add the HF with the aim to remove silica from the carbon in order to increase its surface area, and chemical activation with H$_3$PO$_4$. Furthermore, the modified carbon through ultrasonic irradiation. Characterization of the surface of activated carbon is done through the analysis of XRD and XRF, characterization of functional groups by FTIR, surface area determination by the method of methylene blue, as well as the specific capacitance measurement with CV. The results showed the addition HF can remove carbon silica in rice husks. The element largest of the active carbon with ultrasonic wave irradiation is Ca or oxide CaO by 46.43 %, which has a crystallinity of phase with relatively mesoporous carbon pores. The surface area of activated carbon rice husk with irradiation of
ultrasonic waves in optimum condition at a temperature of 30 °C for 60 minutes which is 184.348426 m² / g. The value of the specific capacity of the activated carbon energy storage rice husks with and without irradiation of ultrasonic waves each is 1067.75 nF / g and 622.17 nF / gram.

**Keywords:** Electrochemical energy, carbon nanopor, rice husk, removal silica, activators H₃PO₄, ultrasonic irradiation.

**INTRODUCTION**

Indonesia is one of the developing countries in the world, where the population continues to increase. This increase caused various impacts on aspects of human life. One aspect that is quite affected by the increase in population is the use of energy to support living needs which include the industrial sector, transportation, household, and so forth. This has led to various energy issues, ranging from new energy sources, alternative energy sources, to the development of energy storage. Mobile phones and laptops are an important part of people's lifestyles today where energy storage media are batteries. But with the variety of sophistication possessed by mobile phones and laptops that have sprung up, it has a weakness in the durability of the limited battery and the long charging time of the battery.

One that can be considered to overcome this problem is to use electrochemical capacitors. Electronic capacitors as energy storage devices have been used extensively in the fields of electronics and transportation, such as digital telecommunication systems, computers, laser pulse systems, hybrid electrical vehicles and so on (Zhu et al., 2007).

Materials used to manufacture electrochemical capacitor electrodes include graphene, carbon nanotubes, carbon aerogels, porous carbon and carbon mineral composites (Hu et al., 2006; Zhu et al., 2007; Stoller et al., 2008; Simon and Burke, 2008; Izadi Nakafabadi et al., 2011). However, the preparation process for these types of carbon requires expensive raw materials, non-renewable raw materials, and long preparation procedures that are time-consuming and costly (Wei et al., 2011).

Biomass waste such as agricultural waste is a potential raw material for pore carbon preparation where biomass waste is easily obtained and the price is very cheap with good electrochemical capacity performance. One of the biomass wastes that has the potential as material for pore carbon is rice husk (Wei et al, 2011).

In this study, activated carbon will be made from rice husk material through carbonization, then modified by removing silica contained in rice husk, then activated with H₃PO₄. Then compared with and without the influence of ultrasonic waves. The XRD, XRF, FTIR, CV and methylene blue methods were used to test the carbon characteristics of rice husks after activation.

**MATERIAL AND METHODS**

**Materials**

The materials used in this study were rice husk waste, phosphoric acid (H₃PO₄),
fluoride acid (HF), methylene blue, aquades, aluminum foil, 0.1 M H$_2$SO$_4$, copper wire, platinum wire and and Whatman No. 42 filter paper.

**Tools**

The tools used in this study are teflon, furnace (Muffle type 6000 furnace), Oven (type SPNISOSFD), water bath, magnetic stirrer (fisher type 115), sieve size 50-100 mesh, analytic balance (Shimadzu AW220), IR (Shimadzu, IR Prestige21), XRD (Shimadzu, XRD 6000), XRF, porcelain saucer, plastic spray gourd, Ultrasonic Cleaner (Elasonic S40H), Cyclic Voltammetry (CV), mortar, vacuum pump (Vacuum brand type ME4C), desiccator, porcelain mortal, laboratory glassware, and thermometer.

**The Procedures**

1. **Sample Preparation**

   All tools and materials for the stage in making activated carbon are prepared and are certain to exist. Before starting research, the scales are examined for measurement. Then materials such as H$_3$PO$_4$, and aquades are sure to have sufficient quantity to make activator solutions and washing solutions. Rice husk originating from agricultural waste in Sidrap district was taken to the Hasanuddin University Faculty of MIPA Physics Laboratory. Then the rice husk is cleaned and then dried under the sun which will then be carbonized.

2. **Rice Husk Carbonization**

   As much as 8 g of clean and dry rice husk are put in a porcelain cup and then heated in a kiln at 350 °C for 1 hour under running air conditions. This process will produce carbon / char from rice husk. After carbonization, the carbon produced is cooled and filtered to 100 mesh.

3. **Expenditure silica from rice husk**

   Carbonized carbon is released silica to obtain silica-free carbon. The carbon powder is added to the Teflon container and fluoride acid (HF) is added until all carbon is submerged by HF. Then heated until the silica evaporates, the carbon is weighed until it has a fixed weight (Wei et al., 2011)

4. **Activation**

   In this study, the activation process used is chemical activation, using an activating agent or activator in the form of H$_3$PO$_4$. The sample which has become charcoal is weighed 10 g then immersed in 100 mL of the solution with the concentration of phosphoric acid activating material to be used is 3 M and then given a 24 hour immersion time. After the sample has been soaked then filtered using Whatman 42 paper and dried in an oven at 105 °C until the weight is constant. The activated carbon that has been produced is washed using Akuadest until the filtrate has a neutral pH, measured using universal pH paper. After washing, the activated carbon is then dried in an oven at a temperature of 110 °C to a constant weight (Kurniawan et al. 2014).

5. **Characterization and Analysis of Rice Husk Nanopores Carbon**

   Characterization of nanopore rice husk carbon was carried out by functional group analysis using FTIR, surface characteristics with XRD, XRF, and
6. Determination of Surface Area by Methylene Blue Methods

To determine the surface area of the carbon can be used methylene blue adsorption method. First, the maximum wavelength is determined. In determining the maximum wavelength, a standard solution of methylene blue 4 ppm was made as much as 10 mL, then measured the absorbance at a wavelength between 650-670 nm using a UV-Vis spectrophotometer. The standard methylene blue curve is made based on the absorbance of various concentrations of methylene blue standard solutions 1, 2, 4, 6, 8, and 16 ppm at maximum wavelengths. Carbon is tested to adsorb the methylene blue solution. The sample is made by 0.3 g of carbon stirred with methylene blue 300 ppm (50 mL) for 60 minutes at room temperature using a magnetic stirrer. After stirring, the carbon is then separated from the filtrate. Methylene blue solution after adsorption then measured its absorbance by UV-Vis spectrophotometry to obtain carbon surface area values.

7. Making Carbon Paste Electrode and Electrode Testing with CV

Carbon paste electrodes are made by mixing paraffin and carbon with a ratio of 1: 1 percentage of weight then the ingredients are mixed and stirred until homogeneous using a spatula on the watch glass which is heated on top of the hotplate at ± 50°C. After the mixture becomes homogeneous, then the electrode paste is inserted into the electrode body manually by being bottled while pressed so that it is solid and even and the carbon can enter the electrode body. The electrodes that have been made are then allowed to stand for 24 hours. The carbon paste electrode was then measured for its electrochemical properties using Cyclic Voltammetry. This measurement uses an Edaq potentiostat with three electrodes. Pt electrodes, and Ag/AgCl as reference electrodes and carbon paste electrodes as working electrodes. Scanning testing was carried out at a voltage of -500 mV to 500 mV with a scanrate of 100 mV/s, using 0.1 M H₂SO₄ electrolyte solution.

RESULTS AND DISCUSSION

Rice Husk Carbonization

The first stage in making activated carbon from rice husk begins with the carbonization process. The carbonization process is carried out to get charcoal from rice husks which will be used as raw material for making activated carbon. According to Sitorus (2009), burning rice husks to obtain carbon occurs at a temperature of 200-400°C carbon, the higher the temperature used for carbonating husks, the less the tendency of carbon. The carbonization stage of rice husk in this study was carried out at 350°C, if the temperature was too high the carbon would turn to ash. This carbonization process lasts for 1 hour and there is a lot of smoke. This happens because of the large amount of volatile substances contained in rice husks and evaporates during carbonization. The carbonization process ends when all rice husks turn into black carbon and the smoke coming out is gone. Carbonized carbon is shown in Figure 1.
After the carbonization process ends, the carbon of the rice husk produced is refined using a filter to the size of about 100 mesh. Particle size will affect the surface area of activated carbon produced. Therefore, it is necessary to refine the process with the aim of obtaining uniform size of rice husk carbon.

**Expenditure silica from rice husk carbon**

According to Wei, et al. (2011), removing silica from rice husk carbon will provide an initial structure so that the carbon produced is purer. In this study, silica removal was carried out using 40% HF solution. According to Sun, et al (2001), Chen and Lena (2001), fluoride acid (HF) is a solvent that can dissolve silica. Silica removal is carried out by inserting carbonized carbon in a Teflon container and then adding excess HF then heating it over the hotplate at a temperature of 200°C until SiF₄ evaporates. SiF₄ evaporation in the sample is indicated by the release of white smoke at the time of addition of HF. When the process of removing silica, the carbon sample will look white solid which shows that there is still silica in carbon, therefore the addition of HF continues until white solids are not seen in carbon samples and the emergence of white smoke is also gone and carbon weight is fixed. Here is the reaction (Svehla, G., 1985):

\[
\text{SiO}_2(s) + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}
\]

The principle of SiO₂ concentration in the carbon samples of rice husk namely silica dissolved in HF, therefore the silica content can be determined gravimetrically, by comparing the weight difference before and after the addition of HF. 5 g of rice husk carbon produces 1.3 g of carbon or about 26% initial weight. The carbon produced then analyzed functional groups by FTIR, analyzed the surface compound content with XRF, and analyzed the surface area with the Methylene Blue Method.

**Analysis of Rice Husk Carbon Function Groups Before and After Silica Expenditures**

The FTIR spectrum before and after silica removal is shown in Figure 2. The spectrum shows several functional groups in the sample. In spectrum A and B, the main peak that is believed to be related to the functional group on silica is at wave number 3441.01 cm⁻¹. This peak is a typical peak for stretching vibration of -OH group (hydroxyl group). Thus, in the carbon of rice husk used as a sample it is believed that there is a hydroxyl group, which shows Si-OH or silanol bonds (Lee et al., 2008; Lin et al., 2001), although the hydroxyl groups donated from hydrated water molecules cannot ignored (Daifullah et al., 2003).
Figure 2. Carbon rice husk spectrum (A) before removing silica and (B) after removing silica by adding HF solvent

In sample A, the second peak believed to show the silica functional group on rice husk carbon was peak at wave number 1095.5 cm\(^{-1}\), with a high enough intensity indicating the presence of Si-O-Si siloxane functional groups (Socrates, 1994 and Daifullah et al., 2003), while sample B is gone. The presence of the Si-O-Si function group in sample A is strengthened by the presence of a peak at the wave number 464.84 cm\(^{-1}\), which shows Si-O bonds (Lin et al., 2001 and Lee et al., 2008), and peaks at 798.5 cm \(-1\) arising from the deformation of the Si-O bond on SiO\(_2\) (Lee et al., 2008). Other peaks in samples A and B with significant intensity were found in the 1600-cm \(-1\) region (Lee et al., 2008), this peak shows a stretch vibration C = O from hemicellulose. In samples A and B there is also a phosphate group found in the 500-cm \(-1\) absorption area, the presence of phosphate groups in the sample can also be proved by the results of XRF analysis. From the analysis of the carbon functional groups of rice husk it is known that by removing silica with the addition of HF it will greatly influence the sample functional groups.

Analysis of Rice Husk Carbon Compound Content Before and After Silica Expenditures

Based on Table 1, it can be seen that the carbon of rice husk prior to the release of silica by the addition of HF contains the main components of silicon (Si) up to 99.50%. According to Wen-Hwei (1986) in Jaya (2002), the content of the main oxide compound in the carbon of rice husk is silica (SiO\(_2\)) with an amount of about 86.90–97.30%. The most common value of silica content from husk ash is 94-96% and if the value is close to or below 90% it is likely caused by samples of husks that have been contaminated with other substances with low silica content (Houston, 1972). As for the addition of excessive HF, the SiO\(_2\) content in the carbon sample is gone. And calcium oxide (CaO) compounds that did not exist before are the most abundant compounds. This is due to the addition of HF to carbon samples so that the compounds previously hidden in the carbon pore of rice husk come out so that they are read in XRF analysis, as is the case with compounds that emerge after the carbon has been released silica.
Table 1. Content and Compound of Rice Husk Carbon Oxides Before and After Expenditures of Silica with Addition of HF.

| Compounds | Before removing silica (% b/b) | After removing silica with HF 40% (% b/b) |
|-----------|-------------------------------|----------------------------------------|
| SiO₂      | 99.50                         | -                                      |
| K₂O       | 0.093                         | 5.67                                   |
| CaO       | -                             | 73.86                                  |
| P₂O₅      | 0.35                          | -                                      |
| MnO       | 0.0237                        | 16.27                                  |
| TiO₂      | -                             | 2.52                                   |
| ZnO       | -                             | 0.66                                   |
| Rb₂O      | -                             | 0.411                                  |
| In₂O₃     | -                             | 0.057                                  |
| TeO₂      | -                             | 0.077                                  |
| Sb₂O₃     | -                             | 0.079                                  |
| Nb₂O₅     | 0.0101                        | 0.194                                  |
| MoO₃      | 0.0072                        | 0.057                                  |
| SnO₂      | -                             | 0.068                                  |

Analysis of Carbon Surface of Rice Husk Before and After the Removal of Silica

Measurements of surface area with the Methylene Blue Method that has been done obtained carbon surface area data before the addition of HF and after the addition of HF are shown in Table 2.

Table 2. Carbon Surface Area Before and After Dispensing Silica with Addition of HF

| Sample                          | Surface area (m²/g) |
|---------------------------------|---------------------|
| Carbon before removing silica   | 182.625             |
| Carbon after removing silica    | 182.680             |

Table 2 shows the carbon surface area of rice husks before silica removal is 182.625 m²/g and after silica removal is 182.680 m²/g. From this point it can be seen that by removing silica contained in the carbon of rice husk it will produce carbon rice husk with a larger surface area. Therefore, carbon is released from the carbon silica of rice husk with the addition of HF which is used for the next procedure, which is activation.

Determination of Optimal Time and Temperature of Activation with and without Ultrasonic Wave Irradiation

The optimum time for ultrasonic irradiation is 60 minutes with a surface area of 182.8 m²/g. High irradiation time does not necessarily produce better efficiency, this is because the longer irradiation time can cause damage to the particle structure of the sample. The optimum temperature for ultrasonic irradiation is at 30 °C with a
surface area of 184.27 m²/g. This surface area is higher than the surface area at optimum time irradiation. From these data it is known that the temperature is very influential on the ultrasonic irradiation process.

Characterization of Rice Husk Activated Carbon Function Clusters

The characterization of functional groups of activated carbon in rice husks was carried out by using FTIR instruments to compare functional groups formed on activated carbon of rice husks by irradiation of ultrasonic waves and activated carbon of rice husks without ultrasonic wave irradiation. The IR spectrum of the two samples is as follows:

Figure 3. FTIR spectrum of rice husk activated carbon with and without ultrasonic wave irradiation

Based on infrared spectra of activated carbon treated with and without ultrasonic irradiation showed that the ultrasonic treatment greatly changed the structure of activated carbon which in the spectra given ultrasonic irradiation treatment decreased the intensity of the peaks that appeared and a shift in some wave numbers. In spectra without ultrasonic irradiation there is absorption band at wave number 3394.72 cm⁻¹ which shows stretching vibration of -OH group, at wave number 2360.67 cm⁻¹ and 2326.08 cm⁻¹ which appear due to vibration O=C=O of the CO₂ from the air absorbed by the material. Cluster C = O appears at wave number 1714.72 cm⁻¹. At other wave numbers absorption occurs at wave number 1598.99 cm⁻¹ which is a vibration of the range C=C of the aromatic group and at wave number 1234.44 cm⁻¹ which is the vibration of the CH-OH group in alcohol.

In the spectra of activated carbon with ultrasonic irradiation some peaks at the wave number are almost the same as the carbon irradiated ultrasonic but the intensity of the spectra for carbon with ultrasonic irradiation is lower, as in wave numbers 3441.01 cm⁻¹ which is the -OH group, in numbers wave 2360.87 cm⁻¹ and 2328.65 cm⁻¹ are absorption bands of group O=C=O of CO₂ from air, group C = C in
Characterization of Rice Husk Activated Carbon Compounds

The content of compounds in activated carbon was analyzed using XRF instruments so that the oxide compound content of irradiated activated carbon and activated carbon without ultrasonic wave irradiation was shown in Table 3.

| Oxide compounds | Activated carbon of rice husk without irradiation (%b/b) | Activated carbon of rice husk with irradiation (%b/b) |
|-----------------|----------------------------------------------------------|------------------------------------------------------|
| CaO             | 72.81                                                    | 46.43                                                |
| MnO             | 14.68                                                    | -                                                   |
| P2O5            | 10.59                                                    | 39.06                                                |
| Cl              | -                                                        | 6.39                                                 |
| K2O             | -                                                        | 5.83                                                 |
| Nb2O5           | 0.70                                                     | 0.83                                                 |
| MoO3            | 0.46                                                     | 0.62                                                 |
| Sb2O3           | 0.229                                                    | 0.287                                                |
| RuO4            | -                                                        | 0.220                                                |
| In2O3           | 0.248                                                    | 0.204                                                |
| SnO2            | 0.281                                                    | 0.149                                                |
| Ag2O            | -                                                        | 0.0074                                               |

Table 3 shows the difference in the content of oxide compounds from activated carbon in rice husks treated with and without ultrasonic irradiation, this can be seen from the difference in the percentage of the number of compounds. The carbon without irradiated ultrasonic has the main compound, CaO, which is equal to 72.81% while the activated carbon which is given ultrasonic irradiation is 46.43%. In addition, there are differences in the composition of different compounds from the two samples, on activated carbon with ultrasonic irradiation there are compounds that are not present in the activated carbon without ultrasonic irradiation and vice versa. Both of these differences occur because of the effect of cavitation which causes the formation and breakdown of bubbles due to ultrasonic irradiation treatment which makes the release of active compounds into solvents, and because of the cavitation effect which results in the breakdown of bubbles so that compounds that were in the sample surfaced.

Characterization of Rice Husk Activated Carbon Phase

Phase characterization formed from activated rice from rice husk with and without ultrasonic irradiation was carried out by X-Ray Diffraction (XRD). Active carbon sample in the form of powder. Observation of X-ray diffraction is carried...
out at an angle of $2\theta = 10^\circ - 80^\circ$ with $\lambda$ Cu-ka 1.540600 (Å).

Comparison of the XRD results between the activated carbon of rice husks and ultrasonic irradiation with activated carbon of rice husks without ultrasonic irradiation can be seen in Figure 4.

Figure 4. The diffraction pattern of rice husk activated and without ultrasonic wave irradiation

Figure 4 shows that the peak position of the activated carbon that appears almost the same, around $2\theta = 20^\circ - 33^\circ$ which shows the diffraction pattern of activated carbon which does not show a sharp peak, the peak provides information that the activated carbon is not crystalline, but is amorphous. According to Nasrullah (2014), samples derived from organic or natural ingredients usually have the structure of amorphous solids, and activated carbon in rice husks is also a natural ingredient. However, in other $2\theta$ regions, several sharp peaks appeared which showed the presence of crystals in the material, so that the activated carbon of rice husks by ultrasonic irradiation in crystalline and amorphous forms.

Characterization of Active Carbon Surface Area of Rice Husk

Carbon rice husk that has been activated through treatment with and without ultrasonic irradiation is then re-analyzed its surface area using the Methylene Blue Method. The results of the analysis are shown in Table 4.
Table 4. Active Carbon Surface Area of Rice Husk with and without Ultrasonic Wave Irradiation

| Sample                              | Surface area (m²/g) |
|-------------------------------------|---------------------|
| Activated carbon rice husk (irradiation) | 184.34              |
| Activated carbon rice husk (without irradiation) | 182.85              |

Table 4 shows the surface area produced from the methylene blue test. The value of the surface area of rice husk activated carbon with greater irradiation is 184.34 m²/g rather than the activated carbon of rice husk without irradiation which is 182.85 m²/g, although the difference is not too significant that is only 1.4959 m²/g. This insignificant change is because the activation method used is not in accordance with the temperature conditions of the activator used, so the change in surface area produced is not optimal. According to Ip et al (2008), H₃PO₄ activators are in the activation temperature range of 600 and 900°C without the presence of oxygen. If the activation temperature is not used at this temperature, then the activator cannot react optimally with carbon during the activation process to form pores. Therefore, it is recommended for previous studies to use activators. However, the difference in results, although not significantly different, proves that the provision of ultrasonic wave irradiation treatment affects the surface area of activated carbon.

Characterization of Rice Husk Activated Carbon Storage Capacitance

The electrodes that have been made are shown in Figure 5.

Figure 5. Rice husk activated carbon electrode

The carbon paste electrode was then measured for its electrochemical properties using Cyclic Voltametry. Figure 6 is the potential (mv) and current (nA) curve of the activated carbon electrode with and without ultrasonic irradiation.

Figure 6. Graph of the relationship of current and voltage of electrode of rice husk activated carbon (a) with ultrasonic irradiation, (b) without ultrasonic irradiation.

Table 5 shows the specific capacitance value of the rice husk carbon electrode with larger ultrasonic wave irradiation, which is 1067.75 nF/gram because the carbon surface area given
ultrasonic irradiation treatment is greater due to the number of pores formed by the cavitation effect of ultrasonic irradiation. According to Wydiantoro and Susanti (2013), a high active surface area will result in a greater possibility of transfer of charge on the carbon surface. However, the capacitance value of the resulting carbon electrode is not too optimal when compared to previous studies. This is because when testing with a potentiostat no low to high scanrate variation is given. According to Narendra and Susanti (2012), at the same temperature, the smaller the scanrate the greater the value of capacitance. This happens because the low scanrate protons and electrons have enough time to insert in areas that are difficult to reach. If the stored and given charge gets bigger, the capacitance value gets bigger.

Table 5. Specific Capacitance Value of Active Carbon Rice Husk with and without Ultrasonic Wave Irradiation

| Sample                        | Storage capacitance value |
|-------------------------------|---------------------------|
| Carbon with irradiation       | 1067.75 nF/gram           |
| Carbon without irradiation    | 622.17 nF/gram            |

CONCLUSION

The conclusions obtained from the results of this study are as follows. Addition of HF can remove silica in the carbon of rice husk. The intensity of the activated carbon functional group with ultrasonic wave irradiation increases, such as the –OH function group, aliphatic C-H (from CH₃ and CH₂), C = O (carbonyl) bonds, C-C and C = C bonds, and phenol (C-O) bonds. The largest element content of activated carbon with ultrasonic wave irradiation is Ca or oxide CaO of 46.43%, which has a crystallinity phase with carbon pores belonging to the mesopore. The surface area of rice husk activated carbon with and without ultrasonic wave irradiation at optimum conditions at a temperature of 30°C for 60 minutes is 184,388 m²/g and 182,852 m²/g. The value of the specific capacity of energy storage of rice husk activated carbon with and without ultrasonic wave irradiation is 1067.75 nF/g and 622.17 nF/g, respectively.

REFERENCES

Chen, M., dan Lena, Q. Ma., 2001, Comparation of Three Aqua regia Methods for Twenty Florida Soils, *Soil Science Society of America Journal*, 65 (2); 491.

Daifullah, A.A.M., Girgis, B.S., dan Gad, H.M.H., 2003, Utilization of Agro-Residues (Rice Husk) in Small Waste Water Treatment Plans, Elseiver B.V., 57 (11); 1723–1731.

Houston, D.F. 1972. *Rice Chemistry and Technology*, Minnecosta; America Association of Cereal Ceramic, Inc.

Hu, C. C., Chang, K. H., an Lin, M. C., 2006, Design and Tailoring of the Nanoturbular Arrayed Architecture of Hydrous RuO₂ for Next Generation Supercapacitors, *Nano Letters*, 6 (12); 2690-2695.

Ip, A.W.M., Barford, J.P., McKay, G., (2008), Production and Comparison of High Surface Area Bamboo Derived Active Carbons. *Journal Bioresources Technol.*, 99 (18); 8909-8916.

Izadi, N. A., Yamada, T., Futaba, D. H., Yudasaka, M., Takagi, H., Hatori, H., dan Hata, K., 2011, High-Power Supercapacitors Electrodes from Single-Walled Carbons
Nanoborn/Nanotube Composite, *ACS Nano.*, 5 (2); 811-819.

Jaya, A.T., Ariwibowo, D.S. 2002. *Effects of Addition of Rice Husk Ash on Expansive Soils.* [Http://dewey.petra.ac.id/jiunkpe_bg_201. Accessed on July 28, 2015.]

Lee, E., Shin, D., Kim, H., Koh, Y., dan Jang, J., 2008, Membrane of Hybrid Chitosan–Silica Xerogel for Guided Bone Regeneration, *Biomaterials*, 30 (5); 743-50.

Lin, J., Siddiqui, J.A., dan Ottenbrite, M., 2001, Surface Modification of Inorganic Oxide Particles with Silane Coupling Agent and Organic Dyes, *PolymerAdvance Technology*, 12; 285–292.

Narendra, R., and Susanti, 2012, Thesis: Electrochemical Capacitors from Tungsten Trioxide (WO₃) Materials with Gel Cell Method and Calcination Process, Department of Materials and Metallurgical Engineering, Sepuluh November Institute of Technology: Surabaya.

Nasrullah, M., and Darminto, Phase Analysis and Width of Carbon Energy Band Gap in Coconut Shell Heating, *Pomits Journal of Art and Science*.

Simon, P., dan Burke, A., 2008, Nanostructured Carbons: Double Layer Capacitance and More, *The Electrochemical Society Interface.*, 38-43.

Socrates, G. 1994. *Infrared Characteristic Group Frequencies.* England: The University of West London.

Stoller, M. D., Park, S., Zhu, Y., An, J., dan Ruoff, R. S., 2008, Graphene-Based Ultracapacitors, *Nano Letters.*, 8 (10); 3498-3502.

Sun, Y.C., Chip, P.H., dan Shiue, M.Y., 2001, Comparison of different Digestion Methods for total Decomposition of Siliceous and Organic Environmental Sample, *Analytical Sciences*, 17 (12); 1395-1399.

Svehla, G., 1985, *Vogel Part II Textbook The fifth edition of Qualitative Inorganic Analysis of Macro and Semimicro*, PT. Kalman Media Pustaka, Jakarta.

Wei, X., Xiao, Li., Jin Zhou, dan Ping, Z. S., 2011, Nanoporous Carbon Derived from Risk Husk for Electrochemical Capacitor Application, *Advanced Materials Research*, 239-242; 2101-2106

Widiantoro, A.T.T., and Susanti, 2013, Effect of Calcination Temperature Variations on the Capacitive Properties of Tungsten Oxide Electrochemical Capacitors (WO3) Sol Gel Synthesis Results, *Technical Journal of POMITS*, 2 (1); 3.

Zakir, M., 2013, Electrodeposition of Ru and Polyaniline Metals on Active Carbon Surfaces of Rice Husk by Ultrasonic Irradiation, *Indonesia Chimica Acta*, 6 (2); 2.

Zhu, Z., Hu, H., Li, W., dan Zhang, X., 2007. Resorcinol Formaldehyde Based Porous Carbon as an Electrode Material for Supercapacitors, *Carbon*, 45; 160-165.