Rubber fruit shell: agricultural waste material as a potential sustainable production for wastewater treatment

Muhammad Naswir¹*, Yasdi¹, Siti Rahima¹ and Yudha Gusti Wibowo²

¹Department of Engineering, Universitas Jambi, Jambi, Indonesia
²Department of Environmental Science, Universitas Jambi, Jambi, Indonesia

*Email: m.naswir@yahoo.com

Abstract. Water quality is a problem in recent decades, rubber fruit shell in agricultural waste will be a solution to solve wastewater treatment. Rubber fruit shell has dried by sunshine for three days and crushed using crusher until the material becomes ash, ash has sifted in 80 and 120 mesh. Ash burned in 400°C and 500°C, ash has activated use acid activator (H₃PO₄) 10% for 24 hours, and then carbon cleaned by aquades till the pH is seven. Then, carbon has dried in oven for 3 hours with temperature 110°C. Specification test using gravimetric method has used to find water concentration and ash content in rubber fruit shell. Titration test used to find adsorption of iodine (mg/g), spectrophotometry UV-VIS used to find adsorption of blue methylene with a wavelength of 560.50 nm, blue methylene has used too for finding a surface area. Freundlich and Langmuir isotherm model has used to find best isotherm model. The isotherm model suitable for adsorption this time is the Freundlich isotherm model because it has a linear line equation that is \( y = 0.4784x + 3.3971 \) with the correlation coefficient \( (r) \) is 0.9922

1. Introduction

Water quality in the world continues to decline, some activities give an impact for water quality caused by human activities such as mining industry [1], domestic waste and disaster. Hydrological and hydrogeological cycle has described that water is never increased or decrease, water have a problem with quality. Decrease of water quality will give an impact for human health [2], environment [3] included animal [4]. Wastewater has some parameters that dangerous for many aspects such as low pH, high heavy metals (Fe, Mn, Mg, Al, Cd, Cu, Cr, Zn, Pb, etc.), high BOD, COD, and TSS [4, 5, 6, 7].

Recent study informs that wastewater treatment using activated carbon. Activated carbon is adsorbent material widely used for water purification [3], contaminated sediment remediation [8], heavy metals treatment [9] and organic pollutant removal [10]. Recent study informs that activated carbon produced by coconut shell. This study will create activated carbon using rubber fruit shell to reduce heavy metal in wastewater. Rubber fruit shell is a potential waste material to create activated carbon using acid activator. Thus, this paper will give solution for wastewater treatment and rubber waste.
2. Method

2.1. Preparation of rubber fruit shell
Rubber fruit shell has dried by sunshine for three days and crushed using crusher until the material becomes ash, ash has sifted in 80 and 120 mesh. Ash burned in 400 °C and 500 °C, ash has activated use acid activator (H3PO4) 10% for 24 hours, then, carbon cleaned by aquadest till the pH is seven. Then, carbon has dried in oven for 3 hours with temperature 110°C.

2.2. Specification test and characterization of rubber fruit shell
Specification test using gravimetric method has used to find water concentration and ash content in rubber fruit shell. Titration test used to find adsorption of iodine (mg/g), spectrophotometry UV-VIS used to find adsorption of blue methylene with a wavelength of 560.50 nm, blue methylene has used too for finding a surface area. Rubber fruit shell has grouped by four samples with different temperature and particle size. Sample 1 using 400°C with 80 mesh particle size, sample 2 using 400°C with 120 mesh particle size, sample 3 using 500°C with 80 mesh particle size and sample 4 using 500°C with 120 mesh particle size. Rubber Fruit Shell has characterization by Fourier Transform Infrared (FT-IR) for before and after treatment.

3. Results and discussions

3.1. Water content test
Water content is a parameter of activated carbon caused by temperature and pyrolysis time. Gravimetric method used to find water content of activated carbon (Figure 1). Water content test is an important test for product control of activated carbon [12], high water content could make low sorption of biochar, it caused by pores of biochar has full of water.

![Figure 1. Water content test of activated carbon.](image)

3.2. Activated carbon ash test
Ash test function determines the content of metal oxides in activated carbon. Ash content in activated carbon caused by mineral on rubber fruit shell. Several studies inform low ash content have a different result on surface properties in activated carbon. Activated carbon has different content of ash in every treatment (Figure 2), increased ash content is due to the presence of non-carbon compounds that attach to the surface of activated carbon. The non-carbon compound is an impurity that covers the pores of activated charcoal and if the amount exceeds the quality standard it will reduce the effectiveness of the absorption process.
3.3. Iodine adsorption

Iodine sorption by activated carbon (Table 1) gives information that the higher pyrolysis temperature and the smaller particle size will lead to a better adsorption process, recent study gives the same information about temperature and particle size. Low iodine absorption is caused by the number of contaminants that are still attached to the surface of the activated carbon which still has not had time to evaporate when the carbonization process takes place.

| No | Samples  | Sorption of Iodine (mg/g) |
|----|----------|--------------------------|
| 1  | Sample 1 | 4854                     |
| 2  | Sample 2 | 5080                     |
| 3  | Sample 3 | 5606                     |
| 4  | Sample 4 | 5681                     |

3.4. Blue methylene sorption

Blue methylene test used to find pores size of activated carbon, blue methylene test has chosen because this test is a low-cost method than use scanning electron microscope. Absorption analysis of methylene blue using absorbance data obtained from reading the UV-VIS Spectrophotometric test filtrate with a wavelength of 560.50 nm. Adsorption of methylene blue influenced by particle size and pyrolysis temperature (Table 2).

| No | Number of Samples | Methylene Blue Sorption (mg/g) |
|----|-------------------|-------------------------------|
| 1. | Sample 1          | 18.2                          |
| 2. | Sample 2          | 18.4                          |
| 3. | Sample 3          | 18.7                          |
| 4. | Sample 4          | 18.8                          |

3.5. FT-IR test

FTIR studies of this adsorbents help in the identification of various forms of the minerals present. FT-IR test has used for characterization before and after treatment using H3PO4. Comparison of wave numbers of carbon absorption bands from rubber shells before and after activated use 10% of H3PO4
(Figure 3 and Figure 4) have different wave, it caused by activating agents can cause a shift in wave number and intensity based on their chemical environment. The OH function group has a shift in the larger wave number and the smaller the intensity after activation.

3.6. Adsorption test of Fe content

The standard iron metal solution is made from a mother liquor of 1000 ppm Fe and then diluted into a standard 100 ppm Fe solution. Then in two standard Fe solutions with various concentrations of 1 ppm; 2 ppm; 3 ppm; 4 ppm; 5 ppm; 8 ppm to create calibration curve. that the calibration curve has a linear line equation that is \( y = 0.0405x + 0.0193 \) with the coefficient of correlation \((r) = 0.9961 \) (Figure 5). On the calibration curve, the absorbance is directly proportional to the concentration of the standard solution, namely the greater the concentration used, the greater the absorbance.
Determination of the optimum contact time of rubber fruit shell activated carbon in this study was determined by a variation of 30 minutes, 60 minutes, 90 minutes and 120 minutes. Then activated carbon with a mass of 0.5 gram is used in the concentration of iron (III) 100 ppm. Effect of optimum contact time for Fe adsorption (Table. 3)

| No | First Concentration (mg/L) | Last Concentration (mg/L) | Time Contact | Efficiency (%) |
|----|-----------------------------|----------------------------|--------------|----------------|
| 1  | 100                         | 58.8                       | 30           | 41             |
| 2  | 100                         | 48.6                       | 60           | 51             |
| 3  | 100                         | 41                         | 90           | 59             |
| 4  | 100                         | 41.6                       | 120          | 58             |

Maximum adsorption happened in 90-minute contact with efficiency 59% and decrease in 120 minutes contact, it caused by adsorbent has reached maximum point for sorption of Fe. Pores of adsorbent has closed by molecular layer, it makes the adsorption capacity has run out [11]

3.8. Efficiency sorption of Fe

Adsorption events occur because the surface of the carbon experiences a force imbalance, consequently the surface of the adsorbent easily attracts another substance, so that the equilibrium is reached. The activated carbon adsorption power is caused by activated carbon having large amounts of pores after going through the pyrolysis process and the activation process that makes the carbon pores more open. The mechanism in the adsorption event is that the adsorbate molecules diffuse through the boundary layer on the outer surface of the adsorbent, some of which are adsorbed and some are left in the solution. If the adsorption capacity is still large, most of it will be absorbed on the surface of the adsorbent.
Table 4. Sorption of Fe by activated carbon

| No | First Concentration (mg/L) | Last Concentration (mg/L) | Time contact | Efficiency (%) |
|----|-----------------------------|---------------------------|--------------|----------------|
| 1  | 20                          | 2.13                      | 90           | 89             |
| 2  | 40                          | 7.08                      | 90           | 82             |
| 3  | 60                          | 15.69                     | 90           | 74             |
| 4  | 80                          | 24.56                     | 90           | 69             |
| 5  | 100                         | 31.32                     | 90           | 68             |

3.9. Adsorption isotherm

Adsorption isotherm of chemical analysis are divided into two such as Langmuir and Freundlich [12]. Sorption of Fe were analyzed by the Freundlich (Figure 5) and Langmuir (Figure 6) at different temperature and particle size.

![Figure 6. Ce/Qe VS Ce.](image)

The value of linearity (R²) is the number of Freundlich isotherm with its linear line equation that is $y = 0.4725x + 0.4007$ with the value $R^2 = 0.9944$. However, for the Langmuir isotherm model the linearity number is not much different from the Langmuir isotherm linearity number, namely $R^2 = 0.9396$. Therefore we calculate the average relative to other criteria to determine which is most appropriate for this adsorption process.

Table 5. ARE of Langmuir and Freundlich

| Average Relative Error (ARE) (Langmuir) |
|-----------------------------------------|
| No  | Co (mg/L) | Ce (mg/L) | Qe   | Qem | Are   |
|----|-----------|-----------|------|-----|-------|
| 1  | 20        | 2.13      | 3.574| 1.126| 68.495|
| 2  | 40        | 7.08      | 6.584| 1.470| 77.677|
| 3  | 60        | 15.69     | 8.862| 1.584| 82.127|
| 4  | 80        | 24.56     | 11.088| 1.621| 85.378|
The smallest number is in the Freundlich isotherm model of 13.888 (Table 5). Then it can be said that the right isotherm model of the adsorption this time is a model of Freundlich isotherm. The Freundlich isotherm model shows that the adsorbate layer formed on the surface of the adsorbent is multilayer. This is the same as the characteristics of physical adsorption which is where adsorption can occur in many layers.

4. Conclusions
The best water content of activated carbon is found in carbon with a size of 120 mesh and a temperature of 500°C of 4.1%, the best ash content is in carbon size 80 mesh and a temperature of 400°C of 0.5%. The best absorption of iodine is in carbon with a size of 120 mesh and a temperature of 500°C of 5681 mg/g. Best absorption of methylene blue is found in carbon with a size of 120 mesh and a temperature of 500°C of 18.8 mg/g with a surface area of 69565.27 m²/mg. It can be concluded from the results of the following data that rubber fruit shells include effective raw materials as the basic ingredient in making activated carbon. Characterization of activated carbon test on FTIR showed significant changes before and after activation by H₃PO₄. OH before activation has a wave number 3410.15 with an intensity of 2.43 having changed after being activated to 3448.72 and its intensity is 1.356. This shows that after being activated the levels of H₂O in carbon are getting smaller so that the carbon absorbing power increases. Another functional group found in carbon from rubber fruit shells is C-C. On the activated carbon, the functional group C-C has a wave number 2337.72 and has an intensity of 8.47 and after activation the fixed wave number is 2337.72 but the intensity decreases to 5.462. Iron (III) ion adsorption test in solution obtained the optimum contact time obtained at 90 minutes with adsorption efficiency of 59%. Furthermore, the variation in Fe concentration is 20 ppm; 40 ppm; 60 ppm; 80 ppm and 100 ppm were found that the higher the concentration, the smaller the adsorption efficiency due to activated carbon which has reached equilibrium. The highest adsorption efficiency was at a concentration of 20 ppm at 89% and the lowest adsorption efficiency at a concentration of 100 ppm, which was 68%. The isotherm model suitable for adsorption this time is the Freundlich isotherm model because it has a linear line equation that is $y = 0.4784x + 3.3971$ with the correlation coefficient ($r$) is 0.9922 compared to the Langmuir isotherm model so that the Freundlich isotherm type is more appropriate for characterizes the iron ion adsorption mechanism by activated carbon.

Reference
[1] Paulus G K, Hornstra L M, Alygizakis N, Slobodnik J, Thomaidis N and Medema G 2019 The impact of on-site hospital wastewater treatment on the downstream communal wastewater system in terms of antibiotics and resistance genes Int. J. Hyg. Environ. Health 0–1
[2] Hao Z, Wang C, Yan Z, Jiang H and Xu H 2018 Magnetic particles modification of coconut shell-derived activated carbon and biochar for effective removal of phenol from water *Chemosphere* **211** 962–9

[3] Benstoem F, Becker G, Firk J, Kaless M, Wuest D, Pinnekamp J and Kruse A 2018 Elimination of micropollutants by activated carbon produced from fibers taken from wastewater screenings using hydrothermal carbonization *J. Environ. Manage.* **211** 278–86

[4] Irvan I, Trisakti B, Sidabutar R, Lubis AH, Cahyani SE, Zusri AS and Daimon H 2020 Combination of CSTR and membrane process in treating palm oil mill effluent (POME) *AIP Conf. Proceed.* **2197** 110003

[5] Irvan, Trisakti B, Nainggolan RM, Hasibuan R and Daimon H 2019 Study of gravity thickener as sludge separator in fermentation of palm oil mill effluent to biogas at pilot scale *AIP Conf. Proceed.* **2085** 020027

[6] Irvan, Trisakti B, Sosanty F and Tomiuchi Y 2016 Effect of discontinuing sodium bicarbonate on fermentation process of palm oil mill effluent *Asian J. Chem.* **28** 377-380

[7] Trisakti B, Irvan, Zahara I, Taslim and Turmuzi M 2017 Effect of agitation on methanogenesis stage of two-stage anaerobic digestion of palm oil mill effluent (POME) into biogas *AIP Conf. Proc.* **1840** 7

[8] Payne R B, Ghosh U, May H D, Marshall C W and Sowers K R 2017 Mesocosm Studies on the Efficacy of Bioamended Activated Carbon for Treating PCB-Impacted Sediment *Environ. Sci. Technol.* **51** 10691–9

[9] Inyang M, Gao B, Yao Y, Xue Y, Zimmerman A R, Pullammanappallil P and Cao X 2012 Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass *Bioresour. Technol.* **110** 50–6

[10] Matos J, Laine J and Herrmann J M 2001 Effect of the type of activated carbons on the photocatalytic degradation of aqueous organic pollutants by UV-irradiated titania *J. Catal.* **200** 10–20

[11] Suzuki M 1994 Activated carbon fiber: Fundamentals and applications *Carbon N. Y.* **32** 577–86

[12] Polovina M, Babić B, Kaluderović B and Dekanski A 1997 Surface characterization of oxidized activated carbon cloth *Carbon N. Y.* **35** 1047–52