Utilization of Rubber Fruit Shells as Activated Carbon for Color Waste Management of Palembang Songket Crafts

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Abstract. This study aims to determine the characteristics of activated carbon from rubber fruit shell and its potential to adsorb color waste produced by Songket craft home industry in Palembang city. This study applied varied carbonization temperature i.e. 500°C, 550°C, 600°C, and 650°C and different activators: KOH and H₃PO₄. Data obtained from this research were then compared to Indonesian National Standard and Indonesian Industry Standard. Findings show that the optimum content of moisture, ash, volatile matter, and fixed carbon obtained from sample which is carbonized at 650°C and activated by 20% KOH are 1.09%, 3.55%, 30.17%, and 66.28%, respectively. Its optimum ability to adsorb iodine, methylene blue, and benzene are 201.25 mg/g, 19.26 mg/g, and 13.32%. This activated carbon can adsorb procion blue about 2.31 mg/g. This study suggests a new recommendation to combine this activated carbon with zeolite in a particular formulation to improve its ability to adsorb dye waste produced from Palembang Songket crafts.

1. Introduction
Palembang is famous for Songket crafts. This craft produces byproduct in the form of dye liquid waste at coloring process which has concentration above a predetermined threshold. This dye pollution varies in type and amount. The most widely used dyes in Palembang are blue procion, naphthol anilid saure and indigosol. Environmental pollution can be caused by this dye liquid waste so it is necessary to remove this contaminant before the waste is discharged into water through biological or chemical process. Utilizing adsorbent is one of method to overcome this problem. Adsorbent is porous solid materials which can absorb particular components contained in fluid. There are two types of adsorbent namely polar and non polar adsorbent. Polar adsorbents are silica gel, alumina, and zeolite while non polar adsorbents are polymer and activated carbon.

Activated carbon has a fairly high surface area ranging from 100-2000 m²/g. Activated carbon can be used as a dye adsorbent, phenol adsorbent [14], and ions such as copper and iron ([19], [2]), supercapacitors [22] and play a role in purifying liquid fume [11].

In general, activated carbon is made from coal and biomass. Biomass is more developed because it is a renewable and cheaper material such as coconut shell ([11], [14], corn stalks [19], cassava skin waste [18] and cane pulp [2].
Rubber plants are one type of plants that can be used as activated carbon starting from wood [22] to rubber fruit shells [21]. Vinsiah, Suharman, and Desi [21] used 7% phosphoric acid as an activator in the processing of activated carbon but the absorption capacity of activated carbon against iodine and methylene blue did not meet the Indonesian National Standard 06-3730-1995. Desi and Lesmini [5] use phosphoric acid which has varying concentrations of 2%, 4%, 6%, 8% and 10% but the absorption capacity of methylene blue has not met SII. Therefore, it is necessary to vary the type and concentration of activator to obtain activated carbon which meets the Indonesian national standards and then utilized it as an adsorbent of waste resulted from Palembang Songket craft production.

2. Method
This study varies three variables namely carbonization temperature: 500°C, 550°C, 600°C, dan 650°C, type of activators, and activator concentration. Concentration of H₃PO₄ are 8%, 9%, 10%, and 11% while concentration of KOH are 5%, 10%, 15% and 20%. This study consisted of 5 stages, namely pre-treatment, carbonization, activation, characterization, and absorption test on dye waste produced by the Songket industry.

2.1. Research procedure
Rubber fruit shell sample were derived from PB 260 species found in Lorong Sarjana Indralaya. The rubber fruit shell is dried for further carbonization in the furnace at 500°C, 600°C, and 700°C for ± 1 hour. The resulting carbon is mashed and then sieved. Carbon is activated using two types and varied concentration of activators namely H₃PO₄ and KOH for 24 hours to form pasta. The pasta is then washed with distilled water until the washing water is neutral. Then the activated carbon produced is dried at 105 °C to remove the water content. Design of this study can be seen in figure 1. Testing of physical and chemical properties of activated carbon aims to determine the quality of activated carbon. Testing of activated carbon properties can be seen in figure 2.

Figure 1. Flowchart of research process

Figure 2. Flowchart of testing of activated carbon characteristics
Water content can be measured by heating 1 gram of sample in a porcelain dish at 150°C for 3 hours. Similarly, volatile matter content can be determined by heating 1 gram of sample in the oven at 900°C for 5 minutes. Activated carbon is expected to absorb iodine and methylene blue by 750 mg/g and 120 mg/g, respectively. The stages of iodine and methylene blue adsorption tests can be seen in figure 3 and 4, respectively.

Figure 3. Flowchart of iodine adsorption test

The stages of benzene adsorption test can be seen in figure 5 while steps of adsorption test on liquid waste Songket crafts is showed in figure 6.

Figure 5. Flowchart of benzene adsorption testing

Figure 6. Flowchart of activated carbon adsorption on dye waste
2.2. Data Analysis

2.2.1. Water content analysis
Water containing in activated carbon can be measure using equation:
\[
\% \text{ water content} = \frac{\text{initial mass of sample (g)} - \text{mass of dried sample (g)}}{\text{initial mass of sample (g)}} \times 100\% 
\]  
(Source: [20])

2.2.2. Volatile matter content analysis
Volatile matter containing in activated carbon can be measure using equation:
\[
\% \text{ Volatile Matter Content} = \frac{\text{initial mass of sample (g)} - \text{mass of dried sample (g)}}{\text{initial mass of sample (g)}} \times 100\% 
\]  
(Source: [20])

2.2.3. Ash content analysis
Ash content can be measure using equation:
\[
\% \text{ Ash Content} = \frac{\text{mass of ash (g)}}{\text{mass of sample (g)}} \times 100\% 
\]  
(Source: [20])

2.2.4. Fixed carbon content analysis
It can be determined using this equation:
\[
\% \text{ fixed carbon} = 100\% - (\text{volatile matter} + \text{ash})\% 
\]  
(Source: [20])

2.2.5. Analysis of activated carbon adsorption on methylene blue and dye waste
Activated carbon adsorption on methylene blue and dye waste can be analyzed using equation:
\[
Q = \frac{C_0 - C_1}{M} \times V 
\]  
(Source: [20])

Q, activated carbon adsorption (mg/g), C_0, initial concentration (mg/L), C_1, final concentration (mg/L), M, amount of sample (g), and V, volume (L).

2.2.6. Analysis of activated carbon adsorption on benzene
Activated carbon adsorption on benzene can be analyzed using equation:
\[
Q = \frac{(b-a)}{a} \times 100\% 
\]  
(Source: [4])

Q, activated carbon adsorption (%), a, mass of activated carbon before adsorbing, and b, mass of activated carbon after adsorbing.

2.2.7. Iodine number
Iodine number can be analyzed using equation:
\[
E = \frac{A - (DF)(C)(BE I_e)(V_{filtr})}{m_{sample}} 
\]  
(Source: [4])

E, iodine number (mg/g), A, initial iodine concentration, C, filtrate concentration (N), BE, equivalent mass, and DF, dilution factor.
3. Results and Discussion

This study obtained data related to content of water, ash, volatile matter and fixed carbon in activated carbon and its ability to adsorb methylene blue, iodine, benzene, and dye waste: blue procion.

Data derived from this study is shown in table 1 and 2.

| Table 1. Activated carbon adsorption and characteristics using H₃PO₄ activator |
| Parameter | Carbonization (°C) | H₃PO₄ Concentration (%) |
|-----------|-------------------|------------------------|
| yield (%) | 500               | 74.02                  |
|           | 550               | 87.71                  |
|           | 600               | 86.52                  |
|           | 500               | 8.35                   |
| Water content (%) | 550 | 2.76               |
|           | 600               | 2.42                   |
|           | 500               | 1.76                   |
| Ash content (%) | 550 | 2.01               |
|           | 600               | 2.23                   |
| Volatile Matter content (%) | 500 | 76.48               |
|           | 550               | 58.18                  |
|           | 600               | 56.98                  |
| Fixed Carbon content (%) | 500 | 23.56               |
| Adsorption on Iodine, mg/g | 500 | 117.08              |
|           | 550               | 167.56                 |
|           | 600               | 170.62                 |
| Adsorption on methylene blue, mg/g | 500 | 9.45                |
|           | 600               | 10.98                  |
| Adsorption on benzene, mg/g | 500 | 6.87                |
|           | 600               | 7.98                   |

(73x279)Parameter | Carbonization (°C) | KOH Concentration (%) |
|-----------|-------------------|------------------------|
| yield (%) | 500               | 82.69                  |
|           | 550               | 93.19                  |
|           | 600               | 83.81                  |
|           | 500               | 11.22                  |
| Water content (%) | 550 | 5.92               |
|           | 600               | 3.13                   |
|           | 500               | 1.81                   |
| Ash content (%) | 550 | 6.34               |
| Volatile Matter content (%) | 550 | 65.44               |

(Sources: [1], [9], [17])
### 3.1. Pre-treatment stage

The pre-treatment stage is needed to reduce impurities and moisture contained in rubber fruit shells. The pre-treatment process consists of three stages: cleaning of rubber fruit shells from adhered dirt using water and brush, drying in the sun, and oven at 110°C for 1 hour. The oven is needed to remove water contained in rubber fruit shells. The results show that the percentage of water-free rubber fruit shells is about 80.83%.

### 3.2. Carbonization stage

Matter will be converted into carbon in the carbonization. A combustion is a rapid reaction of a compound with oxygen gas accompanied by the release of heat and light [8]. Carbonization is incomplete combustion that will produce CO or carbon [8]. Incomplete combustion reactions:

\[
\begin{align*}
\text{C}_{n}\text{H}_{2n+2} + \text{O}_2 & \rightarrow n\text{CO} + (n+1)\text{H}_2\text{O} \\
\text{C}_{n}\text{H}_{2n+2} + \text{O}_2 & \rightarrow n\text{C} + (n+1)\text{H}_2\text{O}
\end{align*}
\]

After the carbonization ends, the carbon produced is refined using 120 mesh filter. The particle size will affect the surface area of activated carbon. Therefore, it is necessary to refine the activated carbon in order to get a smaller and more uniform carbon size. Miranti (2012) suggests that smaller sizes will further expand the carbon surface area during the activation process so that it is expected that during the activation process more pores will form. The more pores formed, the greater surface area of activated carbon.

### 3.3. Activation stage

The chemical activation involves adding activating agents to the carbon produced from carbonization. The activator used was H₃PO₄ with a concentration of 8%, 9%, 10%, and 11%. Acidic activating agents such as H₃PO₄ are better used for lignocellulose material because the lignocellulose compound contained in rubber fruit shells has higher oxygen content and an acidic activating agent can react with oxygen-containing functional groups [10]. At temperatures above 600°C, H₃PO₄ reacts with carbon to produce more pore formation and eliminate P₄, CO₂, H₂O and other volatile matters as in the following reactions [12].

\[
\begin{align*}
5\text{C(s)} + 2\text{P}_2\text{O}_5(l) & \rightarrow \text{P}_4(g) + 5\text{CO}_2(g) \\
2\text{H}_3\text{P}_2\text{O}_7(l) & \rightarrow \text{P}_4(g) + 6\text{O}_2(g) + 2\text{H}_2\text{O}(g)
\end{align*}
\]

This is consistent with findings showing less yield after activation (see figure 7 and 8). In addition organic compounds and substances that are relatively difficult to evaporate on the activated carbon

| Temperature | Fixed Carbon content (%) | Adsorption on Iodine, mg/g | Adsorption on methylene blue, mg/g | Adsorption on benzene, mg/g |
|-------------|--------------------------|---------------------------|-----------------------------------|-----------------------------|
| 500         | 32.88                    | 156.90                    | 19.97                             | 2.07                        |
| 550         | 33.16                    | 183.75                    | 19.93                             | 15.81                       |
| 600         | 40.38                    | 240.64                    | 15.81                             | 6.69                        |
| 650         | 58.84                    | 206.66                    | 13.01                             | 8.92                        |
| 500         | 156.90                   | 133.70                    | 19.97                             | 11.51                       |
| 550         | 168.12                   | 243.34                    | 19.97                             | 12.29                       |
| 600         | 205.41                   | 243.34                    | 19.97                             | 12.61                       |
| 650         | 159.40                   | 201.25                    | 19.97                             | 13.32                       |

(Sources: [3], [7], [13], [16])
will be bond to activator molecules, H$_3$PO$_4$ or KOH, and will come out with the activator during washing of the activated carbon to gain pH 7.

3.4. Characterization stage

The purpose of this stage is to determine physical and chemical properties of rubber fruit shell activated carbon in terms of percentage of water, ash, volatile matter, fixed carbon, and its ability to adsorb benzene, iodine and methylene blue.

3.4.1. Water content analysis

The method used to determine water content in activated carbon is thermogravimetric. Based on SNI 06-3730-1995, the maximum standard of water contained in activated carbon is 15%. The percentage of water contained in activated carbon can be seen in figure 9 and 10.

Figure 9 and 10 show that water contained in activated carbon is about 1-11%. This shows that all activated carbon samples have met SNI 06-3730-1995. Sample which is carbonized at 500°C and activated by 5% KOH has the highest water content about 11.22% while sample which is carbonized at 650°C and activated by 20% KOH has the lowest water content about 1.09%. Water content in activated carbon increases as the concentration of activator rises because of hygroscopic properties factor [15]. However, water content continues to decrease along with a reduce in H$_3$PO$_4$ and KOH concentration and an increase in carbonization temperature. This may be due to less optimal washing process of activated carbon after being soaked with activator so that the impurities react easily with activator which has lower concentration than higher concentration.
3.4.2. Ash content analysis
Ash content is the number of ash produced from the combustion of organic materials. Ash is minerals contained in a substance in the form of Si, Al, Ca, Mg, Na and K [21].

Figure 11 and 12 show that ash content ranges from 1.5-3.5%. Based on SNI 06-3730-1995, the maximum percentage of ash contained in activated carbon is 10%. The amount of ash content tends to increase in accordance with activator concentration addition because there are more impurities or tar bound to activator. These impurities are undissolved in water, so they are still remained in activated carbon although they have taken washing process.

3.4.3. Volatile matter content analysis
Volatile matter content analysis aims to determine the amount of compounds that have not evaporated in carbonization process but vaporized at 900 C. The components contained in the activated carbon are water, ash, fixed carbon, nitrogen and sulfur. Nitrogen and sulfur are volatile components especially when temperatures above 900 C.

The graphs (figure 13 and 14) show that the percentage of volatile matter tends to decrease due to various carbonization temperature factors. The more higher carbonization temperature, the less volatile matter contained in the activated carbon. Volatile matter content ranges from 30.17% to 76.48% for different activators and various carbonization temperature.

3.4.4. Fixed carbon content analysis
Fixed carbon percentage is affected the amount of volatile matter and ash contents. If these substances become more greater, the number of fixed carbon will lower. Figure 13 or 14 show a reduce of volatile matter content and figure 11 or 12 show a slight increase of ash content. As a result, the number of fixed carbon will increase showing in figure 15 and 16.
3.4.5. Iodine adsorption test

This test aims to determine the ability of activated carbon to absorb small molecules or micropores that are not more than 1 nm. The method used in this test is an iodometric titration method that uses iodide ion as a reducing agent. Based on SNI 06-3730-1995, the minimum absorption capacity for activated carbon is 750 mg/g or according to SII 0258-79, the minimum absorption capacity for activated carbon is 200 mg/g. Data on absorption of activated carbon against iodine can be seen in figure 17 and 18. 

Based on figure 17 and 18, the absorption ability of activated carbon to iodine is higher in accordance with the increase in activator concentration, where the highest iodine absorption value is about 243.34 mg/g for sample activated by 15% KOH. This is because with increasing activator concentration, more pores are formed so that the absorption of activated carbon also increases. Pambayun, et al [14] states that concentration of activating agents affects the surface area of activated carbon. Activator functions as solvent of organic compounds or tar which cover the carbon pores, so the increase of activating agent concentration will dissolve more organic minerals and tar.

In this study, the absorption data of activated carbon to iodine has not met the standards determined by SNI that is 750 mg/g but has met the standards determined by SII which is 200 mg/g. The low absorption of iodine by activated carbon is more due to the number of contaminants that are still attached to the surface of activated carbon during the washing process because these contaminants are difficult to dissolve in water. There is a reaction between activators and metals found in carbon to form compounds that are not soluble in water during washing [6]. As a consequence, the ability of activated carbon to absorb iodine is low due to the closure of pores cavity of activated carbon by contaminants or the surface of pores cavity to be more shallow and wide.
3.4.6. Methylene blue adsorption test
This test aims to determine the adsorption ability of activated carbon to molecules with sizes larger than 1 nm. Based on the SII standard, the minimum adsorption of activated carbon against methylene blue must be achieved is 120 mg/g. Methylene blue is used as a parameter to measure the ability of carbon to absorb molecules that have a greater weight. Activated carbon ability to absorb methylene blue can be seen in figure 19 dan 20.

Improper size of pores cavity causes difficulties for activated carbon to adsorb molecules which has similar size to methylene blue. The molecular structure of methylene blue is much larger compared to iodine, while the size of pores cavity produced by activated carbon is still not large enough to accommodate methylene blue molecules.

3.4.7. Benzene adsorption test
This test aims to determine activated carbon ability to adsorb 0.5 nm molecules. Activated carbon should be able to adsorb benzene at a minimum of 25% according to SNI 06-37301995, but the results are still far from the standard (see figure 21 and 22). The maximum percentage of benzene that can be adsorbed by sample carbonized at 550°C and activated by 20% KOH is 15%. This can be caused by only few of pores of activated carbon with a size of 0.5 nm or more are formed. Also, activated carbon pores might be covered by other impurities.

3.5. Blue procion adsorption test
A sample used for next step; dye waste (blue procion) adsorption test, is carbon which is carbonized at 650 °C and activated by KOH. This selection is made base on its fixed carbon content and capability to adsorb iodine, methylene blue, and benzene. The concentration of blue procion that can be absorbed
by sample activated by 10%, 15% and 20% KOH are 1.58 mg/g, 1.89 mg/g, and 2.31 mg/g, respectively.

Findings show that the increase of activator concentration accommodates activated carbon to improve its ability to adsorb blue procion. However, the amount of its adsorption is still low because the pore size of activated carbon formed during the carbonization and activation processes is still not large enough to adsorb molecules which has similar size to blue procion. Moreover, all of dyes can pass macropores part easily as well as mesopores but they are difficult to cross micropores part in activated carbon.

4. Conclusion
Findings show that the optimum content of moisture, ash, volatile matter, and fixed carbon obtained from sample which is carbonized at 650°C and activated by 20% KOH are 1.09%, 3.55%, 30.17%, and 66.28%, respectively. Its optimum ability to adsorb iodine, methylene blue, and benzene are 201.25 mg/g, 19.26 mg/g, and 13.32%. This activated carbon can adsorb procion blue about 2.31 mg/g. This study suggests a new recommendation to combine this activated carbon with zeolite in a particular formulation to improve its ability to adsorb dye waste produced from Palembang Songket crafts.

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