# Characteristics of Activated Carbon from Melinjo Shells Composed of $TiO_2$ Nanoparticles

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**Abstract**. The synthesis of activated carbon derived from biomass melinjo shells has been carried out by compiling it with $TiO_2$ nanoparticles. $TiO_2$ nanoparticles are used to improve the performance of adsorbents as degradation compounds. The main objective of this study was to determine the effect of $TiO_2$ nanoparticles on the activated carbon composite. Activated carbon is first made by carbonizing biomass at 400ºC for 15 minutes, then chemically activated with 65% KOH and physical activation at 500ºC. $TiO_2$ nanoparticles were dissolved in demin water and TEOS produced a mixture of sol and then composite with activated carbon 10 g, 20 g, 30 g, and 40g. The characteristics test which analyzes includes iodine number, XRD, SEM-EDX, and BET tests. Analysis of the largest iodine and surface area (BET) tests is at AC40 each 467.387 mg/g and 273.664 $m^2$/g. The XRD showed that the activated carbon was amorphous while the composite produced a crystalline structure.

## 1. Introduction

Melinjo seeds are usually used as a base for making chips and additives in vegetables. Utilization of melinjo seeds leaves melinjo shells that have not been used and thrown away. The structure of the melinjo shell is similar to peanut shells which have been widely used as activated carbon ie cellulose, hemicellulose, and lignin which indicate that the melinjo shell has the potential as an active carbon material. Data from the Central Statistics Agency (BPS) in Indonesia melinjo production in 2016 reached 203,625 tons [1]. The weight of melinjo shells is around 15% of the weight of the whole melinjo, so the quantity of melinjo shell waste in Indonesia reaches 30,500 tons per year.

The activated carbon content is 87-97% carbon and the rest is hydrogen, oxygen, sulfur, and other materials. The physical properties of activated carbon are determined by the pore size and surface area. Activated carbon has a surface area ranging from 500-1500 $m^2$/g and pore volume ranging from 0.7 to 1.8 $cm^3$/g [2] [3]. Proper pore size distribution is needed to facilitate the adsorption process by providing adsorption sites and appropriate channels for transporting adsorbates. Adsorption increases if the pore diameter is 1-5 times greater than the diameter of the adsorbate [4].

The process of activated carbon adsorption occurs in two stages. The initial stage occurs quickly then the second stage slowly decreases the adsorption capacity because the adsorbate in the adsorbent is saturated so that the adsorbent can no longer adsorb [5]. Therefore it is necessary to do degradation of the adsorbate to overcome the saturation of adsorbents. One method of degradation that can be developed is the process of photocatalysis with semiconductor materials.

Several studies have shown that nano particles are good adsorbents for gas purification such as $TiO_2$ and MgO. Research by [6] [7] investigated the potential of $TiO_2$ and activated carbon as a buffer to adsorb some organic compounds, such as CO, nicotine, and pyridine from cigarette smoke. [8] also observed that there was a decrease in CO gas concentrations of 91.50% and $NO_2$ by 95.40%, in the exhaust gas emissions using activated coconut shell carbon which was inserted with $TiO_2$ while the coconut shell activated carbon media without $TiO_2$ insertion could only reduce CO of 83.10% and $NO_2$ of 93.60%. Another study by [9] examined activated carbon made from palm shell which is composed of $TiO_2$ can increase the surface area of activated carbon by 8.9 $m^2/g$.

Research on the use of melinjo shells as activated carbon is still rare, even though it has great potential. Likewise, $TiO_2$ composites with activated carbon derived from organic compounds such as coconut shell have been done, but activated carbon from melinjo shell waste has never been done. Research by combining activated carbon from melinjo shell with $TiO_2$ is expected as alternative to learning about activated carbon.

## 2. Methods

The materials used in this research were melinjo shells, sodium thiosulfate ($Na_2S_2O_3$), potassium iodide (KI), iodine ($I_2$), starch indicator, KOH and aquadest. The equipment used in this study is the furnace, desiccator, Erlenmeyer, burette, oven, stirrer, funnel, measuring flask, beaker glass, filter paper and statif.

Activated carbon preparation: Melinjo shell waste is washed with distilled water to remove surface impurities and dried. The sample was carbonized in temperature of 400$^oC$ the furnace for 15 minutes. The sample is then crushed and sifted so that the raw material with small particle size (± 200 mesh) is obtained. Then mixing with a activating agent KOH 65%. The variation of mixing activating agent with raw material is 4/1 soaked for 24 hours then stirred at 110 rpm at ± 110$^oC$ for 5 hours. Then dried with an oven at 110$^oC$ for 2 hours to release the water content. Physical activation is carried out at 500$^oC$ for 1 hour. The resulting product is rinsed with distilled water to a pH of around 7. Activated carbon is then dried at 120$^oC$ for one hour to release water content.

AC-$TiO_2$ composite: The composite process refers to [30]. Activated carbon made from melinjo shells is composed with $TiO_2$ Degussa P-25 to increase adsorption ability. 3 grams of $TiO_2$ nano particles are dissolved in 300 ml of demin water then sonicated for 30 minutes. After sonification, 3 ml of TEOS sol was added to the $TiO_2$ solution. TEOS is used as an adhesive between $TiO_2$ and activated carbon. An amount of activated carbon was added to the $TiO_2$-TEOS sol.

**Table 1**. Variable amount of activated carbon to the composite

| Sampel | $TiO_2$ (g) | Activated Carbon (g) |
|---|---|---|
| AC10 | 3 | 10 |
| AC20 | 3 | 20 |
| AC30 | 3 | 30 |
| AC40 | 3 | 40 |

Composites were sonified at 100$^oC$ for 30 minutes then dried in the oven at 120$^oC$ for 4 hours. Characteristics of activated carbon: The iodine test was carried out to determine the active surface area of activated carbon based on the absorption of iodine in solution.

$$I_{absorb} = \frac{\left(H - \frac{b \times a}{Ni}\right) \times 126.9 \times N}{W} \tag{1}$$

with volume of filtrate (H), volume of titrant (b), normality of $Na_2S_2O3$ (a), normality of $I_2$ (Ni), normality of $Na_2S_2O_3$ (0.1 mgrek / mL) (N).

Calculation of surface area before and after composite were analyzed using the Brun-nauer-Emmett-Teller (BET) method, XRD, and SEM-EDX. The instrument that used in BET method is the Autosorb Quantachrome Instruments Nova 3200e surface area analyzer with nitrogen as a gas analyzer.

## 3. Results and Discussion

### *3.1. Analysis of Iodine Number*

One parameter that is analysis and becomes a reference for the quality of activated carbon is absorption capacity $I_2$. The increasing Iodine number, the absorption capacity of Iodine will be even greater, this means that the quality of activated charcoal will be better in absorbing [10] because the use of activated carbon is generally as an absorbent material. The results of this test can be seen from table 2. From the analysis of iodine, activated carbon and composites of activated carbon - $TiO_2$ did not have a significant difference. Samples produce iodine number in the range 400-470 mg/g lower than the standard iodine number for activated carbon 750 mg/g [11]. Activated carbon produced from this study still does not meet the standards the Indonesian Industry Standards. This can be caused by imperfect lignization.

**Table 2**. Iodine number of composites

| Sample | Iodine Number (mg/g) | Surface Area ($m^2$/g) |
|---|---|---|
| Activated Carbon | 421.1 | 254.8 |
| AC10 | 438.9 | 264.0 |
| AC20 | 465.3 | 270.3 |
| AC30 | 452.8 | 268.5 |
| AC40 | 467.4 | 273.7 |

### *3.2. Analysis of Surface Area (BET)*

The area of pore surface is a very important parameter in determining the quality of an activated carbon as an adsorbent. This is because the pore surface area is one of the factors that influence the adsorption power of an adsorbent [10]. The greater the absorption capacity produced, the greater the ability of adsorption of activated carbon [12]. The results of surface area analysis can be seen in table 2. The largest surface area produced in the AC40 sample is 273,664 $m^2$/g. The surface difference between samples is not large. The low surface area is due to the low iodine test results

### *3.3 Analysis of XRD*

The characteristics of using XRD to determine the success of activated carbon composites with $TiO_2$ through the 2θ angle that appears and know the crystallinity that has formed. The XRD results for all samples are obtained as in Figure 1. From the results of XRD activated carbon has an irregular shape, wide and not sharp. This shows the structure of activated carbon has low crystallinity or amorphous. While the XRD results on activated carbon and $TiO_2$ composites show the peaks in the same pattern producing a sharp peak structure that characterizes the formation of high crystallinity. The presence of $TiO_2$ is shown by peaks of 2θ in 27$^o$ which shows that $TiO_2$ which is compiled has a rutile structure.

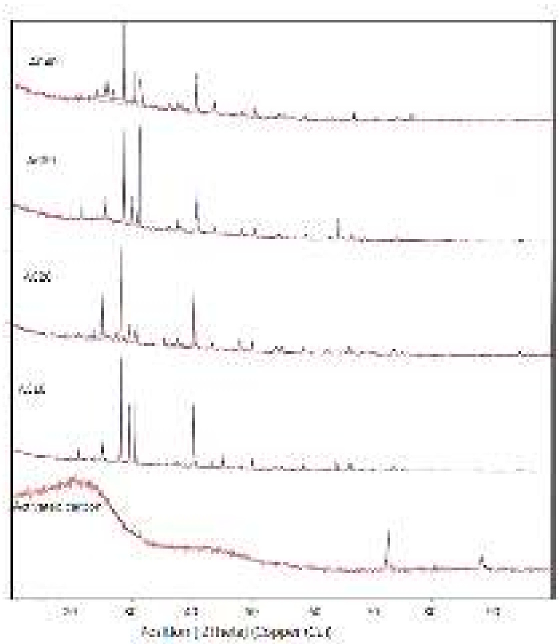
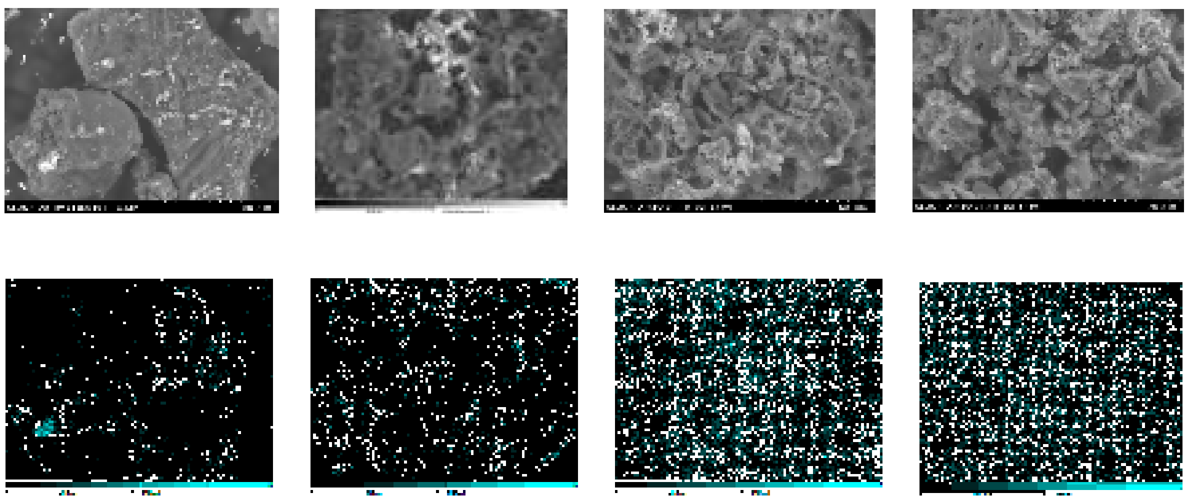


**Figure 1**. Analysis of XRD

### *3.4 Analysis of SEM-EDX*

The distribution of $TiO_2$ in activated carbon is shown in Ti Mapping. Based on Figure 2 the distribution of $TiO_2$ nanoparticles was evenly distributed in AC40 and AC30 samples. In the sample AC10 and AC20 the distribution of $TiO_2$ nanoparticles not evenly distributed, there were several points which tended to accumulate. The amount of activated carbon significantly influences the distribution of $TiO_2$. The results of the study showed that the more activated carbon, the more evenly distributed $TiO_2$. The EDX point results in table 3 show the composition of active carbon and $TiO_2$ composites. The largest composition of $TiO_2$ is in the AC10 sample.



(a) (b) (c) (d)

**Figure 2**. Analysis of SEM (a) AC10 (b) AC20 (c) AC30 and (d) AC40

**Table 3**. EDX composition for KA-$TiO_2$ composites

| Element | Weight% | | | |
|---|---|---|---|---|
| | AC10 | AC 20 | AC 30 | AC 40 |
| C K | 96.91 | 97.41 | 98.46 | 96.70 |
| Si K | 1.07 | 0.95 | 0.50 | 1.97 |
| Ti K | 2.03 | 1.64 | 1.04 | 1.33 |
| Totals | 100.00 | 100.00 | 100.00 | 100.00 |

## 4. Summary
Comparison of the amount of $TiO_2$ and activated carbon affects the results of the composite characterization. The largest surface area is in the AC40 sample 273.7 $m^2/g$ as well as the most even distribution of $TiO_2$ in the AC40 sample. In the XRD test a value of $2\theta$ in $27^o$ indicates the presence of $TiO_2$ compounds in the composite has a rutile structure.

**Acknowledgement**
The authors thank the Indonesian Ministry of Education and Technology for funding all of this research. This research has been awarded a 2019 research funding grant from the Indonesian Ministry of Education and Technology.

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