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Preparation and Characteristics of Kluwak Shell Carbon Adsorbent

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ABSTRACT

Kluwak shell carbon (KTK) is a biomass with potential as an adsorbent, containing cellulose, hemicellulose, lignin, and fixed carbon at a content of 92.15%. However, the current utilization of KTK in adsorbing free fatty acids and methylene blue is limited and can be improved through thermal activation at a range of temperatures. The study aims to investigate the impact of activation temperature on CEC by examining the adsorption capacity of methylene blue solution, iodine solution, and surface area. Activation was carried out for 2 hours at temperatures ranging from 500 to 900 C on Kluwak shell carbon. The adsorbent performance of the activated KTKAT was initially tested using methylene solution with a concentration of 50 ppm, a volume of 50 ml, and 0.15 grams of KTKAT. The solution was placed in an orbit shaker for 90 minutes and filtered. The absorbance of the filtrate adsorption results was measured at a wavelength of 662 nm using UV VIS. For the second test, 50 ml of 0.1 N Iodine and 0.5 g KTKAT were stirred for 15 minutes and then centrifuged for approximately 15 minutes. A volume of 10 ml of the resulting iodine solution adsorption filtrate was titrated with 0.1 N Sodium Thiosulfate. The surface area was determined using the BET method. The concentration (ppm) of methylene blue solution was determined by converting the absorbance measurement using the standard curve equation. The iodine number was determined by titrating the iodine adsorption filtrate with sodium thiosulfate (ml). These data show that there is an obvious correlation between activation temperature and methylene blue absorbance, iodine number, and surface area. At 800°C, the methylene blue adsorption is 12.41 mg/g, the iodine number is 875.61 mg/g, and the surface area is 561.404 m^2/g.

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1. INTRODUCTION

Adsorption is a purification process that involves a driving force between a liquid or gas and a solid, resulting in the formation of a thin layer or film on the surface of the adsorbent. The process of adsorption or absorption involves two components: (1) the adsorbate, which is a liquid or solution that is absorbed, and (2) the adsorbent, which is a solid material used for absorption. Soluble substances in a solution can be clumped together by adsorbents, either chemically or physically. Activated carbon is the most commonly used adsorbent due to its high adsorption capacity and surface area, which ranges from 100 to 2,000 m^2/g. However, commercial activated carbon can be expensive, so researchers are developing ways to make it from renewable and affordable materials [1]. Biomass contains a significant amount of carbon and is readily available at a low cost. It is a potential solution to the problem of waste generated from agricultural or plantation processes, as it can be converted into a valuable resource. Currently, researchers are focusing on the development of activated carbon derived from biomass due to its renewable and cost-effective nature. Biomass waste such as nut shells, solid waste from pressing grains, pulp, and fruit skins can be used to produce activated carbon. The Kluwak shell is composed of cellulose, hemicellulose, and lignin. According to the proximate test, it has a fixed carbon value of 92.15%, making it a highly promising source of raw material for producing activated carbon [2]. In terms of its adsorption capacity for methylene blue (MB), Kluwak shell carbon (KTK) is 15.27 mg/g [3]. To enhance the performance of adsorbents, they can be activated chemically or physically. This process aims to increase the pore size by oxidizing surface molecules, thereby increasing the surface area and improving the adsorption power.

Physical activation involves flowing activators in the reactor at high temperatures, while chemical activation involves mixing carbon material with activating reagents such as acids, bases, or salts. It is important to note that this improved text adheres to the desired characteristics of objectivity, comprehensibility, logical structure, conventional structure, clear and objective language, format, formal register, structure, balance, precise word choice, and grammatical correctness. in addition, it is important to note that it is not possible to define the exact nature of the activation process. The raw material is heated to 600-900°C under vacuum conditions to produce carbonization results (carbon). Chemical Activation is the process where the carbonized material is mixed with certain chemicals such as KOH, NaOH, H_3PO_4, NaCl, K_2CO_3, and other solutions before heating and then washed to remove the residual chemicals used during the activation process, indicated by the wash filtrate having a pH of 7 [4]. According to [5], the maximum adsorption capacity (qm) for remazol red adsorption using coconut-activated carbon at 900 C increased from 125 mg/g to 222.2 mg/g. Thang N.H's research [6] found that increasing peanut shell carbon activation at 800-850°C increased methylene blue adsorption (mg/g) and specific surface area (m2/g). In this study, we aim to improve the performance of kluwak shell carbon by physically activating it at temperatures ranging from 500-900°C for 2 hours, resulting in the production of temperature-activated kluwak shell carbon (KTKAT) with high absorbency as an adsorbent. This study employs kluwak shells, which have been considered waste for the environment. However, using them as adsorbents provides economic value for kluwak farmers and contributes to waste management with a positive impact on society. Additionally, this knowledge offers an alternative to producing adsorbents from biomass, reducing dependence on coconut shells and improving the availability of sorbents through activation.

The performance of KTKAT adsorbent was tested by adsorbing methylene blue and iodine, both of which indicate the criteria of activated carbon by SNI 06-3730-1995 as well as the adsorbent surface area. The adsorption process of methylene blue (MB) and iodine was used for Kluwak shell carbon (KTK) and temperature-activated Kluwak shell carbon (KTKAT) to determine the improvement of adsorbent performance and the optimal activation temperature. The adsorption power on MB and iodine, as well as the surface area, were determined for various activation temperatures using equation (1) from [7] and [8], and equation (2) according to SNI 06-3730-1995 for iodine number. Surface area analysis was conducted using the Brunauer-Emmett-Teller (BET) method at P/Po 0.05 - 0.3, as determined by equation (3) [9].

1. Adsorvency to Methylene Blue

$$qe_{mb} = \frac{(Co - Ce)}{m} \; x \; V \; \ldots.. (1)$$

2. Absorbency of Iodine

$$qe_{Iodine} = \frac{\left(10 - \dfrac{Vnt \; x \; Nnt}{0.1}\right) x \; fb \; x \; 12.69}{m} \quad \ldots.\ldots (2)$$

3. Surface Area

$$\frac{1}{W\,'\left(\frac{Po}{P}\right) - 1\,'} = \frac{1}{Wm * C} + \frac{C - 1}{Wm * C}\left(\frac{P}{Po}\right) \; \ldots \ldots (3)$$

Description :

Feb = Amount of methylene blue adsorbed per mass of adsorbent at equilibrium, (mg/g; mL/g)
$qe_{Iodine:}$ = Amount of iodine adsorbed per mass of adsorbent at equilibrium (mg/g)
Co = The initial concentration of MB in the solution (mg/L)
Ce = The equilibrium concentration of MB in the solution (mg/L).
Vnt = Volume of sodium thiosulfate during titration
Nnt = Sodium thiosulfate concentration (normality) 0.1 N
FB = Dilution factor (50/10) = 5
m = Weight/mass of adsorbent (g)
P = Adsorption equilibrium pressure (atm)
P^o = Desorption adsorption saturation pressure at cooling temperature (atm)
Wm = Weight of nitrogen gas forming the monolayer (g)
W = Adsorbed weight at relative pressure (P/Po) (g)
C = Energy constant

2. RESEARCH METHOD

2.1 Carbon Fabrication

Sample preparation involved cleaning and drying the kluwak shell until the moisture content reached approximately 15%. The Kluwak shell was then carbonized using a rotary kiln at a temperature of 800°C for 2 hours. After cooling, the carbon was crushed and sieved to a size of 1.7 mm. The resulting carbon was washed and dried to a moisture content of approximately 15%. The carbon was then activated and used as an adsorbent with KTK code.

2.2 Temperature Variation Activation Stage

Kluwak shell carbon (KTK) was activated by heating 50 grams in a porcelain cup in an oven. The temperature was increased slowly by 30-100°C to an activation temperature of 500°C and held for 2 hours. The furnace temperature was then slowly lowered to 25-30°C. The resulting Kluwak shell carbon, code KTKAT1, from the 500°C activation was placed in a desiccator, packaged, and is now ready for use as an adsorbent. The experiment was conducted over a temperature range of 600 to 900°C. The Kluwak-activated shell carbon was classified as KTKAT2, KTKAT3, KTKAT4, and KATKT5.

2.3 Batch System Adsorption Testing

a. Methylene Blue Adsorption

The following steps were taken to conduct methylene blue adsorption testing:

1) 0.15 g of kluwak shell carbon (KTK) was placed in a 100 mL Erlenmeyer flask.
2) 50 mL of methylene blue solution with a concentration of 50 ppm was added to the flask.
3) Steps 1 and 2 were repeated for KTKAT1, KTKAT2, KTKAT3, KTKAT4, and KTKAT5.
4) The six samples were shaken for 90 minutes at 250 rpm using an orbital shaker. The filtrate was then analyzed using UV-VIS at a wavelength of 662 nm after filtration.

b. Iodine Adsorption:

1) Altogether 0.5 g of Kluwak shell carbon was placed in a conical flask and 100 mL containing 50 mL 0.1 N KI was added.
2) The same treatment was repeated for KTKAT1, KTKAT2, KTKAT3, KTKAT4 and KTKAT5.
3) The six were also treated by stirring for 15 minutes and then centrifuged for 15 minutes to separate the filtrate.
4) 10 mL of the filtrate was taken and titrated with 0.1 N sodium thiosulfate solution until the filtrate turned the same yellow color.
5) Apply 1 mL of Amylum solution at 1% concentration and titrate with sodium thiosulfate until the blue color disappears.
6) Record the volume of sodium thiosulfate (in mL) used for titration and calculate the Iodine absorption using Equation (2).

2.4 Surface Area Testing

The surface area (A) was determined using a surface area analyser (SAA) of type TouchWin version 1.2x with the BET method. The BET method is based on the relationship of P/Po and $\frac{1}{W'\left(\frac{Po}{P}\right)-1}$, against the amount of adsorbed gas. This method is commonly used to determine the specific surface area of a material.

2.5 Data

1. **Standard Curve:**

Methylene blue solutions were prepared at concentrations of 0, 1, 2, 3, 4, 5, and 6 ppm in 50 mL volumes, fig 1. Absorbance was measured at a wavelength of 662 nm and plotted against the concentration of methylene blue on the X-axis and absorbance on the Y-axis. The equation for linear regression, Absorbance (Abs) = Slope x Concentration + Intercept, was used to determine the concentration of the adsorption test results and the initial concentration of methylene blue for the six samples based on the research variables. The absorbance measurement results of the standard solutions for six concentrations of methylene blue are shown in Table 1.

Figure 1. Methylene Blue Solution Preparation of Standard Curve

Table 1. Concentration and absorbance of Methylene Blue Solution.

Concentration (ppm)	Absorbance
0	0
1	0.056
2	0.109
3	0.181
4	0.279
5	0.349
6	0.423

2. **Methylene Blue and Iodine Adsorption**

Table 2 shows the results of the Methylene Blue and Iodine adsorption test on Kluwak shell carbon and temperature-activated Kluwak shell carbon. The table indicates the adsorption levels of both substances.

Table 2: Adsorption of Methylene blue and Iodine on KTK and KTKAT

Temperature (C)	Absorbance of Methylene blue	Sodium Thiosulfate Volume (mL)
100	0.850	6.50
500	0.400	6.30
600	0.117	4.80
700	0.030	4.00
800	0.010	3.10
100	0.850	6.50

3. RESULTS AND DISCUSSION

In the Results and Discussion section, a graph was constructed to show the correlation between the concentration (ppm) and the absorbance using the data from Table 1, as shown in Figure 2.

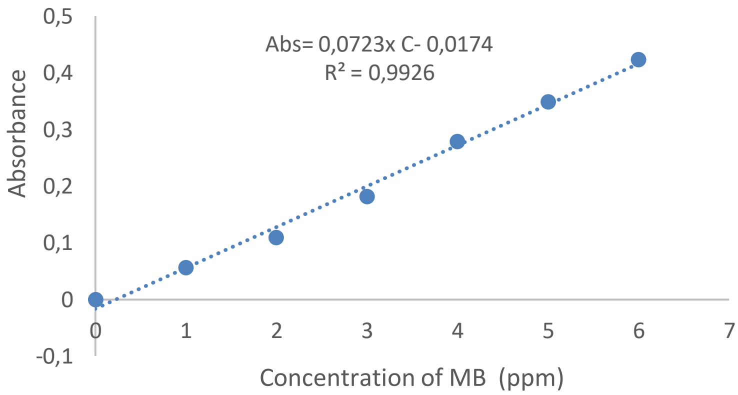

Figure 2. Konsentrasi Larutan Methylene Blue Terhadap Absorbansi

Then, the equation Abs = 0.071 * C - 0.0152 was used to calculate the equilibrium concentration (Ce) of the adsorption results. The value of C is given by Eq. (5).

$$C = \frac{Absorbance + 0.0152}{0.071} \ldots \ldots \ldots (4)$$

3.1 Adsorption of Methylene Blue and Iodine

a. Methylene Blue

In this section, we will determine the concentration of methylene blue adsorbed by kluwak shell carbon and temperature-activated kluwak shell carbon. We have also maintained a logical flow of information with causal connections between statements.

The first step is to determine the equilibrium concentration (Ce) using the modified standard curve liner equation (Equation 2). We can then calculate the amount of adsorbate adsorbed by the adsorbent using Equation (3).

$$CAbsorbed = Co - Ce \qquad \ldots.. (5)$$

The initial concentration of MB was 50 ppm (mg/L), with a volume of 50 mL and a weight of KTK/KTKAT of 0.15 g. The amount of methylene blue adsorbed by the adsorbent is calculated using Equation (1). Table 3 in this section displays the equilibrium concentration and adsorption value of methylene blue.

Table 3. Equilibrium Concentration and Adsorption Value of Methylene Blue

Activation Temperature (°C)	ABS	Concentration (ppm / mg/L)		Methylene Blue Adsorption Quantity qe (mg/g)
		Equilibrium Concentration (Ce)	CAbsorbed (C)	
100	0.850	11.443	38.557	9.639
500	0.400	5.507	44.493	11.123
600	0.117	1.773	48.227	12.057
700	0.030	0.625	49.375	12.344
800	0.010	0.361	49.639	12.410
900	0.004	0.282	49.718	12.429

The increase in activation temperature resulted in a higher concentration of methylene blue being adsorbed by the kluwak-caged carbon adsorbent. This suggests that new pores are formed during activation, leading to changes in the material's physical properties. The increase in methylene blue adsorption capacity indicates an increase in surface area. Table 3 shows that KTK has an MB adsorption power of 9,639 mg/g, while the average KTKAT adsorbs 12,052 mg/g, indicating a 26.84% increase in performance for the adsorbent activated at 500-900°C. The equilibrium adsorption of methylene blue (qe) is similar between activation temperatures of 800°C and 900 °C, suggesting that activation of KTK > 800 °C is ineffective for pores of the same size, resulting in insignificant additional adsorption capacity. The maximum adsorption capacity value is influenced by the surface area, as shown in Table 4.

b. Iodine

The iodine value indicates the adsorbent's ability to adsorb molecules with a diameter of less than 2 nm or 20 Å, which indicates the type of pore size of the adsorbent. According to IUPAC, diameter and pore size are divided into three categories: micropores with a diameter less than 2 nm, mesopores with a diameter between 2-50 nm, and macropores with a diameter greater than 50 nm. The amount of iodine adsorbed by KTK and KTKAT was determined using Equation (2), and the calculation results are shown in Figure 3.

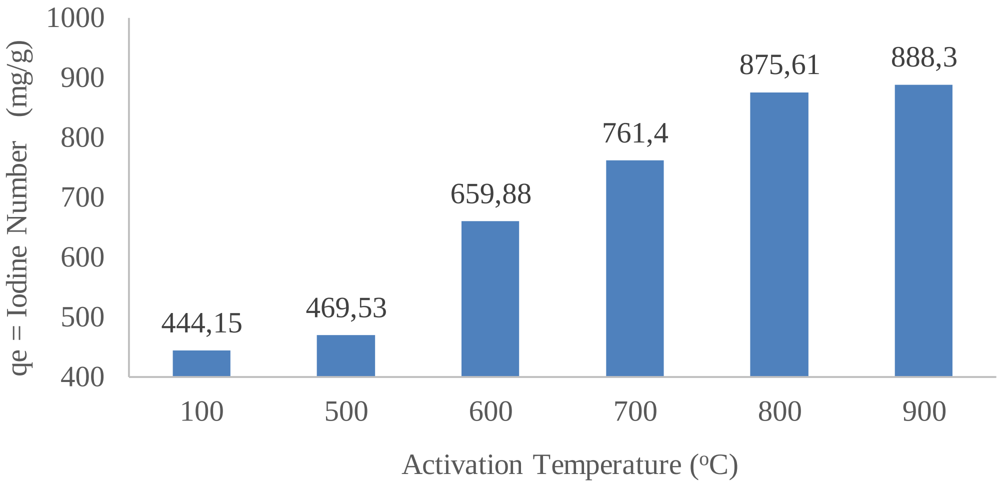

Figure 3. Iodine Absorbency Activation Temperature

The iodine adsorption of KTK and KTKAT with a 50 ml volume of 0.5 g adsorbent increases proportionally with the activation temperature, as demonstrated in Figure 4. The iodine number of KTKAT at 700-900 ^oC meets the SNI 06-3730-1995 standard for activated carbon. This standard requires an iodine adsorption capacity of >750 mg/g for carbon in powder or granular form.

The Kluwak shell carbon (KTKAT) is heated to temperatures between 500 and 900 C. During the activation process, new voids or small pores are created due to the influence of heat. The process of heat activation decomposes volatile compounds, releasing them into the pores and covering the surface, resulting in the formation of new pores. As Handika [10] explains, pores are formed and enlarged due to cellulose degradation and evaporation. According to the research reported by Zakaria [11], activating mangroves as a carbon source at 300°C increased the adsorption capacity of methylene blue to qe of 72.3 mg/g.

c. Surface Area

Surface area properties were determined using the BET tool SAA, represented by P/Po ratio (0.05 to 0.3) and $\frac{1}{W\cdot\left(\frac{Po}{P}\right)-1}$, as shown in Figure 4 for KTK. Table 4 shows the total surface area for the samples based on the research variables. The total surface area (St) is calculated using the relationship between Wm and N (Avogadro's number) with the cross-section of a nitrogen area.

The slope is 16.5146 g^{-1} and the intercept is 4.4380 g^{-1}, in Figure 4, and value $Wm = \frac{1}{Slope + Intercept}$. This gives a Wm value of 0.0477 g with an M (Nitrogen "N_2") value of 28.013 g/mol.

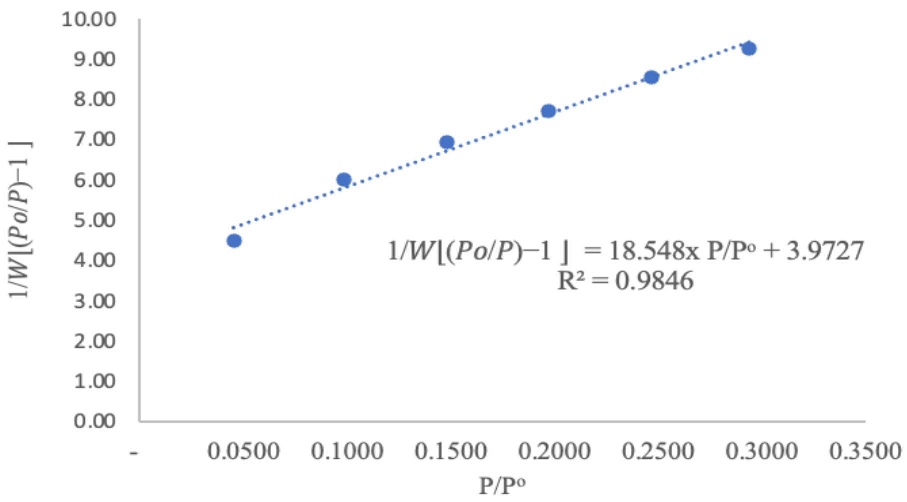

Figure 4. Ratio of P/Po and $\frac{1}{W\left(\frac{Po}{P}\right)-1}$

The surface area of the Kluwak Shell Carbon (KTK) is represented by the variable St, equation (4) :

Error! Digit expected. ………… (6)

$$St = \frac{\left(0.0477\ g\ x\ 6.203\ x\ 10^{23}\ \frac{molekul}{mol} x\ 16.2x10^{-20}\ \frac{m^2}{g.molekul}\right)}{M28.013\ g/mol}$$

$$= 166.2372 \frac{m^2}{g}$$

Table 4. Surface Area Kluwak Shell Carbon (KTK) and Activation Temperature (KTKAT)

No	Code	Temperature °C	Surface Area m²/g
1	KTK	100	166.237
2	KTKA-500	500	229.636
3	KTKA-600	600	404.741
4	KTKA-700	700	461.917
5	KTKA-800	800	561.513
6	KTKA-900	900	541.614

According to Juan Rafael Garcia et al. [12], the activation of palm kernel shells at 500-550°C increases the maximum adsorption capacity for methylene blue sorption (qmax) to 225.3 mg/g and the adsorbent surface area (BET) to 1058 m^2/g. Additionally, the surface area increases, and the total volume of carbon shell kluwak carbonization 800°C activated 600°C is 307.008 m^2/g and 106.4 cm^3/g (Haniffuddin Nurdiansah and Dian Susanti) [13]. According to Table 4, the surface area increased with temperature activation treatment between 500-900 ^{o}C compared to CEC. However, the value of A decreased for the 900^{o}C treatment. This suggests that at temperatures above 800 C for kluwak shell carbon, there is an increase in pore diameter size due to the large amount of heat supplied. This causes the volatile substances between the pores to evaporate, resulting in the merging of two or three pores into one. Kondapalli [14] reported similar research on the activation of fish scales. The study found that at a temperature range of 30-60°C, the maximum capacity of Cr (VI) adsorption increased while the surface area of the adsorbent decreased. Additionally, excess combustion of carbon elements during activation temperatures > 500°C led to the activation of bagasse [15].

4. CONCLUSION

a) The temperature activation of kluwak shell carbon increased the absorption of methylene blue and iodine.
b) The best activation was achieved at 800°C, resulting in a qeMB of 12,410 mg/g, an iodine number of 875.61 mg/g, and a surface area of 561,404 m^2/g.

5. ACKNOWLEDGEMENT

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