Fabrication of Activated Charcoal from Coconut Shell Combined with Coal Fly Ash from PLTU Nagan Raya for Adsorption of Methylene Blue

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Abstract. Coconut shell is one of the abundant agricultural solid wastes in Aceh Province. Meanwhile, a solid waste of coal fly ash is a by-product from PLTU Nagan Raya. Both coconut shell and coal fly ash have a great potential to be utilized as adsorbent. The aim of study is to prepare and characterize the adsorbent made from the combination of coconut shell activated charcoal and coal fly ash. The prepared adsorbent was characterized using Scanning Electron Microscopy (SEM) to study the morphological structure, Fourier Transform Infra-Red Spectrophotometer (FTIR) to detect the functional group and X-Ray Diffraction (XRD) to determine the crystalline structure. Performance of adsorbent was carried out by adsorption process of methylene blue solution on adsorbent. The characterization results showed that all four types of the prepared adsorbents met the requirements of water content quality and iodine adsorption according to SNI 06-3730-1995 concerning to activated charcoal. It was obtained that adsorbent with the best performance was coconut shell activated charcoal (without addition coal fly ash) having the adsorption capacity to methylene blue of 45.36 mg/g on adsorption contact time of 140 minutes.

1. Introduction
Aceh Province is one of the largest producers of coconut shell waste in Indonesia. The existence of coconut shell waste can be minimized by utilizing those agricultural by-product materials as raw material to produce activated charcoal. In addition to reducing waste, producing activated charcoal from coconut shell is a very cost-effective approach compared to the production of activated carbon from coal as a more expensive raw material. It was reported that activated carbon from coconut shell has a high density and purity and harder carbon properties and more resistant to attrition [1]. In addition, coconut shell activated carbon is reported to have an amorphous form, which capable of absorbing various kinds of gases, vapors and colloidal solids [2-4]. In 2015, Roesniani et al [5] used coconut shell waste as a material to produce activated charcoal adsorbent and successfully adsorbed ammonia by 34.87%. Besides source of coconut

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waste, Aceh Province especially in the Nagan Raya Region also generates coal fly ash (FA) waste due to the presence of electrical steam power plant (PLTU Nagan Raya) in surrounding area. Coal fly ash is a by-product as well as the main solid waste produced from the coal combustion process in the industry. If not handled properly, the presence of coal fly ash can damage the land and pollute the environment [6]. Application of coal fly ash as one of the materials for water and wastewater processing can offer great advantages economically and environmentally. Zhao et al [7] modified fly ash with TiO₂ and used it as an adsorbent to remove ammonia. They succeeded in removing ammonia by 79% for 3 hours of contact time [8].

In this study, coconut shell and coal fly ash were mixed to produce a new combined adsorbent. The combined adsorbent with the best characteristics was obtained by studying the appropriate combination ratio of both coconut shell and coal fly ash. The performance of the adsorbent was tested by the adsorption process of adsorbent in methylene blue solution

2. Experimental

2.1 Materials

The used materials were coconut shell, coal fly ash, 0.1 M of H₂SO₄ solution (Merck KGaA), methylene blue (Merck), 0.1 N of iodine solution (Merck), 1% starch indicator, 0.1 N of sodium thiosulfate (Merck) and distilled water.

2.2 Tools

The tools used in this study were Fourier Transform InfraRed Spectroscopy (FTIR) (Agilent Technologies Cary 630 FTIR), Scanning Electron Microscopy (SEM) (JEOL-JSM 6510 LA), X-Ray Diffraction (XRD) (Pan Analytical, Expert Pro), hot plate and stirrer, muffle furnace (Isuzu model EPTR-26R), Spectrophotometer UV-Visible (Shimadzu 1800), digital scales (Mettler PE 300l), mechanical sieves 100-200 mesh (TEST-SIEVE 410-69) and desiccator.

2.3 Preparation of adsorbents

Coconut shell was put into the furnace and then carbonized. Carbonization was carried out at temperature of 400°C for 2 hours [9]. The obtained coconut shell charcoal was then cooled for 24 hours, then milled and sieved using a 100-200 mesh sieving [10, 11]. The same procedure was performed on coal fly ash.

Combination of activated charcoals from coconut shell (TK) and coal fly ash (FA) was prepared with 4 (four) variation mass ratio of 100:0; 70:30; 30:70 and 0:100. A total of 50 grams of combined coconut shell charcoal : coal fly ash were soaked in 500 ml of sulfuric acid solution of 0.1 M for 24 hours then drained. After that, it was filtered and rinsed with distilled water until the pH was close to neutral. It was then placed into a muffle furnace at a temperature of 800 °C for 2 hours [12]. Once finished, the adsorbents were stored in the desiccator.

2.4 Characterizations of Adsorbents

The prepared adsorbents were characterized in terms of their morphological structure, chemical functional groups and crystalline structure using Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red Spectrophotometer (FTIR) and X-Ray Diffractometer (XRD), respectively.

2.4.1 Water content

The adsorbent as much as 2 grams was put into the porcelain dish that has previously been weighed. The dish was placed into an oven at 105°C for 3 hours then cooled in a desiccator and weighed again.

\[
\text{Water Content (\%)} = \frac{a - b}{a} \times 100\%
\]  

(1)
a and b are respective weights of adsorbent before and after drying (g)

2.4.2 Ash content
A total of 2 grams adsorbent was put into a porcelain dish and furnaced at 600 °C for 6 hours. Once done, the adsorbent was cooled in a desiccator. The mass of adsorbent before and after furnaced were weighed to determine the ash content.

\[
\text{Ash Content (\%) = } \frac{a}{b} \times 100\%
\]

(2)

a is the weight of ash (g) and b is the initial weight of adsorbent (g)

2.4.3 Adsorption of Iodine
The 0.15 grams of adsorbent was put into a dark and sealed beaker. Then, 50 mL of 0.1 N of iodine solution was put in the beaker then shaken for 15 minutes then filtered. A total of 10 mL of filtrate was titrated with 0.1 N of sodium thiosulfate solution. When the yellow color of the solution was seen almost disappeared, 1% starch indicator was added. Titration was continued until the blue color was gone.

\[
\text{Adsorption of Iodine (mg/g) = } \left(10 - \frac{N \times V}{0.1}\right) \times 12.69 \times 2.5
\]

(3)

Where, V is the needed volume sodium thiosulfate solution (V), N is the concentration of sodium thiosulfate solution solution (N), S is the weight of carbon (g), and 12.69 is a constant representing the iodine amount corresponding to 1 ml of 0.1 N sodium thiosulfate solution.

2.5 Adsorption of Methylene Blue
A total of 0.1 gram of adsorbent with a combination ratio of 100:0; 70:30; 30:70 and 0:100 was put into an erlenmeyer containing 50 ml of 100 ppm methylene blue solution. Following that, the erlenmeyer was closed and stirred at 100 rpm. The methylene blue solution in the erlenmeyer was then filtered. The concentration of methylene blue in the filtrate was determined by the curve of methylene blue absorbance.

\[
\text{Removal (\%) = } \frac{\text{Initial conc. of Adsorbate} - \text{Final conc. of Adsorbate}}{\text{Initial conc.}} \times 100\%
\]

(4)

\[
\text{Adsorption Capacity = } \frac{\text{Initial conc. of Adsorbate} - \text{Final conc. of Adsorbate}}{\text{Adsorbent amount}} \times V \text{ of sol}
\]

(5)

3. Results and Discussions

Characterization results of combined activated charcoal from coconut shell and coal fly ash is given in Table 1. The characterization of water content was treated by oven at 105°C for 4 hours. Meanwhile, the characterization of ash content was treated by furnace at 600°C for 3 hours. Table 1 shows the analysis results of the combined adsorbent, indicating that the water content and adsorption capacity of iodine have met the activated charcoal quality standard based on SNI No. 06-3730-1995. However, the ash content in the samples with ratio TK:FA of 70:30; TK: FA of 30:70 and TK: FA of 0: 100 have not complied to the SNI quality. This is because the standard quality in terms of ash content for combined activated charcoal from coconut shell : coal fly ash adsorbent is not yet available in the SNI record. In addition, coal fly ash is an ash,
therefore, the higher the composition ratio of fly ash in the combination, the greater the ash content will be. Though the ash content is high, all adsorbents still showed a good iodine adsorption performance. Amongst all, activated charcoal from coconut shell (without addition of coal fly ash) showed the best iodine adsorption ability of 1988.1 mg/g.

Table 1. Characterization results of combined activated charcoal from coconut shell and coal fly ash

| Parameter          | SNI Standard Quality No. 06-3730-1995 | Adsorbent     | Analysis Results |
|--------------------|--------------------------------------|---------------|------------------|
| Water content      | Max. 15%                             | TK:FA 100:0   | 11.55 %          |
|                    |                                      | TK:FA 70:30   | 8.81 %           |
|                    |                                      | TK:FA 30:70   | 0.93 %           |
|                    |                                      | TK:FA 0:100   | 0.12 %           |
|                    |                                      | TK:FA 100:0   | 0.72 %           |
|                    |                                      | TK:FA 95:5    | 9%               |
| Ash content        | Max. 10%                             | TK:FA 90:10   | 18%              |
|                    |                                      | TK:FA 70:30   | 50.25 %          |
|                    |                                      | TK:FA 30:70   | 96.46 %          |
|                    |                                      | TK:FA 0:100   | 99.83 %          |
|                    |                                      | TK:FA 100:0   | 1988.1 mg/g      |
| Iodine absorbancy  | Min. 750 mg/g                        | TK:FA 70:30   | 1692 mg/g        |
|                    |                                      | TK:FA 30:70   | 1692 mg/g        |
|                    |                                      | TK:FA 0:100   | 1607.4 mg/g      |

Note: TK for coconut shell and FA for coal fly ash

Performance on additional samples was also carried out by using two adsorbents with combination ratios of 90:10 and 95:5. The ash content in these additional samples was obtained as much as 18% and 9%, respectively. These results confirmed that the lesser the content of the fly ash in the combined adsorbent, the lower ash content. The ratio TK:FA of 95:5 adsorbent has an ash content which is in accordance with SNI No. 06-3730-1995.

3.1 Scanning Electron Microscope (SEM) analysis
The Scanning Electron Microscope (SEM) analysis was carried out to observe the surface morphology of the prepared adsorbents. The results of SEM imaging can be seen in Figure 1. Based on Figure 1, there are significant morphological differences on the surface of the combined adsorbents. The adsorbent with ratio TK:FA of 100:0 (no addition of fly ash) has larger pores with impurities seen attaching on the surface. Meanwhile, those that combined with fly ash tend to have smaller pores that attributed to the presence of fly ash.

3.2 Fourier Transform Infra Red (FTIR) Analysis
The characterization using a Fourier Transform Infra Red (FTIR) is aimed to observe the functional groups existing in adsorbents prepared from the activated charcoal of coconut shell : coal fly ash. The results of FTIR analysis can be seen in Figure 2.
Figure 1. SEM images of (a) TK:FA of 100:0, (b) TK:FA of 70:30, (c) TK:FA of 30:70 and (d) TK:FA of 0:100 adsorbent at mag. of 2000x

Figure 2. Infrared spectra of combined TK:FA 100:0; TK:FA 70:30; TK:FA 30:70 dan TK:FA 0:100 adsorbents

Based on Table 2, it can be seen that the absorption of the C-H, C = O and Si-O-Si groups dominate the four combined adsorbent samples. From the results obtained there was a decrease in intensity of absorption peak for samples with increased fly ash addition. This shows that the addition of fly ash
to coconut shell activated charcoal affects absorption intensity in wavelength regions and results in changes in functional group structure [14]. In addition, there is a formation of the P-O-C functional group formed on the coal fly ash combined adsorbent due to the presence of P element from fly ash. The absorption band at the wave numbers 3074.53 and 3653.18 cm\(^{-1}\) which is the H-O-H stretch vibration of a water molecule that has a weak hydrogen bond with the Si-O surface on the adsorbent with ratio of TK: FA = 0 : 100.

**Table 2.** Resulting FTIR readings of coconut shell combined with coal fly ash activated carbon sorbent

| Bond  | Reference [13] | TK:FA of 100:0 | TK:FA of 70:30 | TK:FA of 70:30 | TK:FA of 0:100 |
|-------|----------------|----------------|----------------|----------------|----------------|
| P-O-C | 1050-950       | -              | 977.91         | 977.91         | 995.27         |
| C-H   | 3000-2700      | 2758.21; 2872.01 and 2985.81 | 2870.08 and 2985.81 | 2792.93 and 2987.74 | 2856.58 and 2927.94 |
| C=O   | 1900-1650      | 1726.29 and 1759.08 and 1784.15 | 1726.29; 1759.08 and 1784.15 | 1683.86 and 1683.86; 1784.15 and 1791.87 |
| Si-O-Si | 1130-1000   | 1083.99 | 1083.99 | 1082.07 | 1058.92; 1080.14 |
| Si-OH | 3700-3200      | -            | -              | -              | -              |
| Si-H  | 2250-2100      | -            | -              | 2133.27        | -              |
| Al-O  | 570-420        | 493.78 dan 437.84; 455.2 dan 476.42 | 433.98 dan 464.84 | 432.05 dan 478.35 |
| Fe-O  | ≈567           | 588.29      | 588.29         | 588.29         | 580.57         |

3.3. X-Ray Diffraction (XRD) Analysis

The X-Ray Diffraction (XRD) characterization of the coconut shell combined coal fly ash adsorbent was carried out at an angle of 20. The results of the XRD analysis can be seen in Figure 3. Figure 3 presents the results of X-ray diffraction analysis of coconut shell combined with fly ash sample. Activated carbon shows a highly irregular microcrystalline structure in which graphite micro crystals are randomly oriented [15].

![Figure 3. XRD pattern of coconut shell combined coal fly ash activated charcoal adsorbents](image-url)
As in the TK: FA 100: 0 adsorbent contains a slight sharp peak that indicates the presence of SiO2, namely in the region 2θ = 12.97° (d = 6.8242 Å). The slight sharp peak in adsorbent of TK:FA = 100: 0 indicates that this is an amorphous structure [16].

In each adsorbent, some of peaks are detected at a 2θ area of 12.97° (d = 6.8242 Å) (TK:FA of 100:0); 26.82° (d = 3.3241 Å) (TK:FA of 70:30); 26.73° (d = 3.3357 Å) (TK:FA of 30:70) dan 26.63° (d = 3.3473 Å) (TK:FA of 0:100) indicating the presence of SiO2. The emergence of sharp peaks indicating the better alignment of the layers that is the characteristic of the crystal structure [16]. The components found in each type of adsorbent are presented in Table 3.

### Table 3. Analysis results of XRD

| Component | TK:FA of 100:0 | TK:FA of 70:30 | TK:FA of 30:70 | TK:FA of 0:100 |
|-----------|----------------|----------------|----------------|----------------|
| SiO2      | 12.6           | 73.5           | 81.3           | 36.4           |
| C         | 26.2           | 1.1            | -              | 63.6           |
| Al2O3     | 39.2           | 10.2           | -              | -              |
| Fe2O3     | 3.6            | 6.6            | 8.9            | -              |
| TiO2      | 18.3           | 8.6            | 9.8            | -              |

The TK: FA of 70:30 and TK: FA of 30:70 adsorbents had more SiO2 content due to the addition of fly ash. However, at the same time, some components like carbon and Al2O3 actually decreased even disappeared in the TK:FA of 30:70 sample.

### 3.4. Effect of Sorbent Types on Efficiency and Capacity of Methylene Blue Adsorption

The adsorption efficiency of the adsorbent is influenced by several factors, such as contact time. Based on Figure 4, it can be seen clearly that adsorption efficiency increases with increasing contact time between the adsorbate and the adsorbent. The longer the contact time, the concentration of methylene blue decreases until the equilibrium is reached. Based on the results, it was found that the adsorption efficiency for the initial concentration of 100 mg/L with a contact time of up to 140 minutes with sampling every 10 minutes increased. Activated charcoal from coconut shell (TK:FA equal to 100:0) adsorbent has the highest adsorption efficiency up to 97.14%, whereas, adsorbent with combination ratio of TK:FA equal to 30:70 showed the lowest adsorption efficiency of 5.58%. The adsorption rate of the adsorbate is very big during the initial contact time, namely in the 30th minute to the 120th minute. Meanwhile, from the 120th to the 140th minute of adsorption time, the equilibrium was achieved.

The adsorption capacity represents the ratio of the amount of adsorbate absorbed by the adsorbent [17]. The correlation between combination ratio of prepared materials to produce adsorbents to the adsorption capacity can be seen in Figure 5. Figure 5 showed that the longer the contact time between the adsorbent and methylene blue resulted in increasing the adsorption capacity. The highest adsorption capacity was obtained when using only activated charcoal from coconut shell adsorbent that is equal to 45.36 mg/g. Meanwhile, the when using adsorbent with TK: FA ratio of 30:70 showed adsorption capacity of only 2.27 mg/g.

The results showed that the adsorption capacity of adsorbents TK: FA 30:70 and TK: FA 0:100 had the lowest adsorption capacity. This is consistent with the results of the XRD test that showed that no Al2O3 compound was found in the sample. Al-Si-O ion bonds form a crystal structure, which has a cavity structure filled with interchangeable water and cations and has a pore of a certain size that can expand the surface of the adsorbent [18].
Figure 4. The effect of combination ratio of adsorbents on the adsorption efficiency

Figure 5. Effect of combination ratio of adsorbents to the adsorption capacity

4. Conclusion
The combination of activated charcoal from coconut shell with coal fly ash has been successfully carried out with the emergence of a new functional group containing P element in FTIR results. The XRD results revealed that the highest SiO$_2$ content of 81.3% was obtained at ratio sample TK:FA of 30:70. The equilibrium time of methylene blue adsorption using combination of activated charcoal from coconut shell and coal fly ash was reached in minutes 120$^{th}$. The highest removal efficiency of methylene blue was obtained by using activated charcoal from coconut shell. Similarly, the highest methylene blue adsorption capacity was 45.36 mg/g.
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