Characterization of Activated Carbon Prepared From Banana Peels: Effect of Chemical Activators on the Adsorption of Gas Emissions

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Abstract. The aims of the study were to investigate characteristics of activated carbon prepared from banana peels as adsorbent for the removal gaseous emissions from motorcycles. The effect of different chemical activators and contact time were studied on the characteristics of banana peels raw carbon (RC) and chemically activated carbon (CAC) such as moisture content, ash content, volatile matter. The best iodine adsorption capacity of CAC H2SO4 3N 3 hour contact, was obtained at 913.68 mg/g adsorbent. Structure and morphology of RC and CAC were characterized by Fourier transform infrared (FTIR) and field emission scanning electron microscopy (SEM). The results showed that RC and CAC could significantly adsorb the CO and SO2 gases emissions from motorcycles, but not applicable for NO, NOx gases. After 10 minutes analysis using gas emission Analyzer, CO gas could be removed, from initial 16014 ppm to 3578 ppm using CAC H2SO4 adsorbent, while SO2 gas could also be partly removed from 217 ppm to 19 ppm using CAC ZnCl2 adsorbent. Banana peels carbon produced was suitable for application in removing CO and SO2 gases emissions from motorcycles and it helps to reduce the greenhouse gas effects of fossil fuel usage to the environment.

1. Introduction

The production of activated carbon from agricultural byproducts has both economic and environmental effects, as it converts unwanted, low-value agricultural waste to useful high-value (1. Ekpete et al, 2017, preparation).

Activated carbon (AC) has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants from aqueous or gaseous media. It is widely used due to its high surface area, well-developed internal microporosity, and wide spectrum of surface functional groups [1] [2] [3].

Many researchers have reported the production of ACs from various sources of lignocellulosic waste materials including coconut shell and husk, [4] [5] palm oil shells, [6] cotton stalks [7] durian...
shell [8] rice husk, [9] jackfruit peel [10], pomegranate seeds [1] sugar cane bagasse [2], hazelnut shell [3], almond shell [11]. Woods [12], Olive stone [13], date stone [14]. Walnut shell [15] etc.

Banana is one of the world’s most important crops grown by more than 130 countries. India, China, Uganda, Philip-pines, Ecuador, Brazil, Indonesia, Columbia, Cameroon and Ghana were the top ten bananas producing countries in the world in 2012. In India the banana production in 2012 was about 24.9 million tons while the total world production of banana during 2012 was about 139.2 million tons [28,29]. Several research groups have used raw and chemically treated banana peels and banana stalks for the removal of toxic heavy metal and wastewater treatment.

Physical and chemical activation methods are used for preparation of ACs. In physical method, the carbonization of the carbonaceous materials is carried out at high temperature range of 700-1100 °C in inert atmosphere followed by activation with oxidizing gases (activating agents) such as oxygen, steam and CO2. However, in chemical activation the carbonization of the precursor materials is carried out at comparatively low temperature (400-700 °C) in the presence of a chemical activating agent. The carbonization and activation during chemical activation method occurs at the same time.

The advantages of chemical activation method over physical activation are: (i) it is a single step process, (ii) it is carried out at lower temperature and usually have a better effect on pores development, and (iii) high carbon yields and low energy cost [15]–[22]. (Ahmad et al, 2015, Production of AC)

In the chemical activation process, either the previously carbonized product is impregnated with suitable chemical agents, such as acids (HNO3, H2SO4, and H3PO4) or salts (ZnCl2, MgCl2, FeCl3, AlCl3, and K2S). These reagents act by solubilized cellulose, which, at elevated temperatures, separates, as a highly dispersed amorphous carbon, which forms a porous structure in the carbonaceous adsorbent. (Buzcek, 2016, Preparation AC by additional).

Chemical activation is preferred over physical activation owing to the higher yield, simplicity, lower temperature and shorter time needed for activating material, and good development of the porous structure [12]. (Hasyem, 2017)

Along with that, the adsorption capacities of chemically treated agricultural adsorbents are much better than untreated adsorbents [15]. (Ali et al, 2016, Removal of chromium). The main objectives of this work are: (a) to study the effect of various contact times of banana peels activated carbons prepared by characteristics KOH, H2SO4 and ZnCl, activators; (b) to study the effect of chemical activators toward the adsorption of gas emission from motorcycles. The global objective is to show that a common activators or precursors may be used to prepare activated carbons for the removal of CO and SO2 gas emissions. We hope that this research could make a great contribution in reducing motorcycles gas emission effects to human and environment, and likely applicable for adsorption of wastewater and gaseous pollutions.

2. Methodology

2.1 Materials
Banana peels: Banana peel were obtained as waste from local market in Banda Aceh, Indonesia. The peels were used as adsorbent in two different form i.e raw and carbonized activated for the removal of gas emission from motorcycle. Chemicals: Potassium hydroxide, sulphuric acid, zinc chloride and all chemicals reagents used in the titration were analytical grade and supplied by Merck Germany.

2.2 Methods

2.2.1 Carbonization and chemical activation
The banana peels were washed, cut into pieces of ±3 cm and subjected to air for 7 days. The dried peel kept in the oven at 105°C for 24 hour to remove the moisture content. The dried peels were carbonized at box type furnace at temperature of 400 °C for 1.5 hours to become charred or carbon and ground and sieved at 125mm. The carbon namely as Raw Carbon (RC). The raw carbon is activated chemically using KOH, H2SO4 and ZnCl2 3N by soaking 100 g of raw carbon into 300 ml of each activators for 1, 2 and 3 hour contact time, respectively. Chemically activated carbon (CAC) were filtered and washed by aquadest until netral (pH=7), then oven at 200°C for 2 hours. After
cooled, some of CAC powders were separated for physical characteristics and carbon surface morphology using Scanning Electron Microscope (SEM) and Fourier Transform-Infra Red (FT-IR). The remaining CAC were mixed with Amilum for molding as cubicles (1x1x1 cm) and oven heated for 3 h at 120 °C. The CAC cubicles then used for the gas emission adsorption studies.

2.2.2 Moisture content determination
Thermal drying was used in determination of the moisture content. The proximate analysis was done according to standard procedure of Indonesia (SNI No. 06- 3730-1995). The powder sample of RC and CAC were kept in a hot-air oven at 105±2°C till constant weight was obtained. The difference between the initial and final mass of the carbon represents the moisture content. The percentage moisture content (%) was computed as follows:

\[
\text{Moisture}\% = \frac{\text{loss in weight on drying (g)}}{\text{Initial weight (g)}} \times 100
\]  

(1)

2.2.3 The ashes content and volatile matter determination
For ash content determination, crucibles were preheated to about 500°C, then cooled in a desiccator, and weighed. 1.0 g of each sample was transferred into the crucibles and weighed. The crucibles containing the samples were then placed in the furnace and the temperature was allowed to rise to 500°C for about 1 hr 30 min and allowed to cool in a desiccator to room temperature (30°C) and weighed. The ash content was calculated using the equation:

\[
\text{Ash (\%)} = \frac{\text{Ash Weight (g)}}{\text{Oven dry weight (g)}} \times 100
\]  

(2)

For volatile matter determination, 1.0 g of each sample was heated at a temperature of 500°C for 10 minutes. The volatile matter was calculated using the equation:

\[
\text{Volatile (\%)} = \frac{\text{Weight of volatile component (g)}}{\text{Oven dry weight (g)}} \times 100
\]  

(3)

2.2.4 Iodine Number Determination
The parameters that can precisely indicate the quality of low cost activated carbon made of banana peels is the adsorption capacity of the iodine solution. The larger the iodine number of activated carbon, the greater the ability to absorb the solute in the environment. The percent iodine adsorbed by each carbon was calculated by applying the formulabelow.

\[
\left(\frac{\text{mL of Na}_2\text{S}_2\text{O}_3 \text{ in blank} - \text{mL Na}_2\text{S}_2\text{O}_3 \text{ in sample}}{\text{mL of Na}_2\text{S}_2\text{O}_3 \text{ in blank}}\right) \times 100
\]  

(4)

2.2.5 FTIR and SEM analysis
The RC and CAC functional groups on the surface of each carbonized sample were characterized by Fourier Transform Infrared Spectra (FTIR) using Shimadzu IR Prestige, while the morphology of activated carbon characterized using Scanning electron microscope (SEM) JSM Series.

2.2.6 Gasses Emission Adsorption Process
Process of gases emissions adsorption study was accomplished within 2 steps; (1) preparation of the adsorption tube or exhaust model for filling the adsorbents, in cubicles size of 1x1x1 cm; (2) Gases
emissions adsorption study was done on motorcycle Honda Astrea year 2012. Measurement of CO and SO2 gases emission from motorcycle was determined using Flue gas Analyzer 6000 at idle condition, after 0, 5 and 10 minutes analysis. The schematic procedure of adsorption of gas emission from motorcycle describe in Fig. 1. Removal of CO and SO2 gases emission were determined by comparing the analysis value recorded before and after adsorbents filled in the exhaust model, while the motorcycles being accelerated for 10 minutes.

![Figure 1. The procedure of gas emission analyzing using adsorption tube](image)

3. Results and Discussion

3.1 Characteristics of raw and chemically activated carbon (RC and CAC)

The characteristics of carbon produced from banana peel (RC and CAC) highly depends on the preparation and carbonization temperature. The choice of temperature of 400°C was taking into consideration based on the observation made by Sugumaran [3] while working with banana stem. Our previous research also has proven that the best carbonization temperature for preparing carbon from banana peels were at 400°C in the range of 400-700°C (Viena et al, 2017). The physical characteristics of raw carbon also depends on the method of activation (Shown in Table 1 and 2). From the table it could be explained that the contact time may result in the higher Iodine number adsorption by the chemically activated carbon, especially for ZnCl2 activated carbon which could removed the SO2 gas emission 92%. Despite its environmental unfriendliness, chemical activation method has been thriving over physical activation method due to its low energy cost, high carbonyield, and easy recovery process of activating agents. Several activating agent have been reported for use in the chemical activation process. Among them H3PO4 and KOH are widely used in the production of activated carbon because of low energy costs and high carbonyields as well as easy recovery of the activating agents [57-58]. While the general mechanism of the chemical activation are not so well understood asthat of physical activation [59] (Sugumuran, 2012)

| Activators       | Contact time (Hour) | Moisture content (%) | Ash content (%) | volatile matter (%) |
|------------------|---------------------|----------------------|-----------------|--------------------|
| Raw carbon (RC)  | 0                   | 6                    | 5               | 12                 |
| CAC-KOH          | 1                   | 7                    | 4               | 13                 |
|                  | 2                   | 5                    | 2               | 11                 |
|                  | 3                   | 2                    | 3               | 9                  |
| CAC-H2SO4        | 1                   | 12,0                 | 4,0             | 13,0               |
|                  | 2                   | 10,0                 | 2,0             | 11,0               |
|                  | 3                   | 8,0                  | 3,0             | 9,0                |
| CAC-ZnCl2        | 1                   | 10,60                | 6,90            | 9,40               |
|                  | 2                   | 10,70                | 8,30            | 10,30              |
|                  | 3                   | 10,70                | 9,00            | 10,40              |

Table 2. The iodines adsorption of chemically activated carbon at different contact times
### Table 1: Activator Contact time (Hour) Iodine adsorption (mg/g)

| Activator | Contact time (Hour) | Iodine adsorption (mg/g) |
|-----------|---------------------|--------------------------|
| Raw carbon (RC) | 0                   | 662                      |
| CAC-KOH   | 1                   | 817.24                   |
|           | 2                   | 837.54                   |
|           | 3                   | 862.92                   |
| CAC-H2SO4 | 1                   | 837.54                   |
|           | 2                   | 888.3                    |
|           | 3                   | 913.68                   |
| CAC-ZnCl2 | 1                   | 562.76                   |
|           | 2                   | 649.82                   |
|           | 3                   | 785.65                   |

#### 3.2 SEM of banana peel carbon

The surface morphology of the Raw carbon and chemically activated carbon were analyzed using SEM (Scanning Electron Microscopy) at 1000 - 3000X. From Figure 2, it could be shown that the adsorbent pores surface has less opening after being activated by chemicals activators KOH, H2SO4 and ZnCl2 compared to before activation process.

**Figure 2.** SEM results of (A) raw carbon, and chemically activated carbon by (B) KOH, (C) H2SO4 and (D) ZnCl2.

#### 3.3 Functional Groups Identification using FTIR (Fourier Transform Infra Red)

Figure 6 demonstrated the comparison of the wave number of carbon absorption band shell. Before activation frequency of C-H group is in the intensity of 81.23, while the increased intensity after activation of C-H group that is equal to 92.50. The intensity level of C-H functional groups value, were influenced by the content of H2O. The higher the content of H2O, the intensity of C-H group is getting low. Activation temperature has highly effect on the absorbed area of Iodine and the functional group on the surface of banana peels activated carbon.
Figure 3. FTIR analysis banana peels activated carbon before thermal activation (left) and after chemical activation (right).

3.4 Effect of contact time on the gas emission adsorption
The object of our research was the use of banana peels adsorbent (raw and activated) as adsorbent for the removal of gaseous emission from automotive/motorcycles which has been used since year of 2012. The Motorcycle gas emission analysis was accomplished by making a model of adsorbant tube from knalpot that filled with RC and CAC media that has formed into small cubicles shapes of 1x1x1cm. Modified shape of CAC were aims to minimize the destruction of adsorbents pores during the emission test. The CAC formed were arrange layer by layer, which allow the empty space between the adsorbent as the pathway to adsorption process flows during the acceleration of motorcycles movement. These empty space between the activated carbon meant to give better contact and adsorption of gaseous NO, SO, NOx, SOx, CO, HC. The results of the emission analysis was showed in Table 1.

| Activator          | Contact time (Hour) | CO Emission (ppm) | SO2 Emission (ppm) | CO Adsorption Effectiveness (%) | SO2 Effectiveness (%) |
|--------------------|---------------------|-------------------|--------------------|---------------------------------|-----------------------|
| No adsorbent       |                     | 16014             | 217                |                                 |                       |
| Raw carbon (RC)    | 0                   | 13752,00          | 172,00             | 14,13                           | 20,74                 |
| CAC-KOH            | 1                   | 8876,00           | 165,00             | 35,46                           | 23,96                 |
|                    | 2                   | 7781,00           | 129,00             | 51,41                           | 40,55                 |
|                    | 3                   | 5477,00           | 75,00              | 65,80                           | 56,40                 |
| CAC-H2SO4          | 1                   | 8754,00           | 95,00              | 45,34                           | 56,22                 |
|                    | 2                   | 7264,00           | 76,00              | 54,64                           | 64,98                 |
|                    | 3                   | 3578,00           | 46,00              | 77,66                           | 78,80                 |
| CAC-ZnCl2          | 1                   | 9161,00           | 111,00             | 42,79                           | 48,85                 |
|                    | 2                   | 8175,00           | 64,00              | 48,95                           | 70,51                 |
|                    | 3                   | 7686,00           | 19,00              | 52,00                           | 91,24                 |

From Table 1, it could be explained that RC and CAC was a potential media for adsorbing CO and SO2 gases emission, but not for NO and NOx gases, as the parameter keep raising up during the
emission test. Meanwhile, after 10 minutes of flue gas analysis at idle mode using adsorption tube, CO gas could be totally removed, from initial 16014 ppm to 3578 ppm using CAC H2SO4 adsorber, while SO2 gas could also be partly removed from 217 ppm to 19 ppm using CAC ZnCl2 adsorber. These phenomena was caused by the total pores size of RC and CAC particles didn’t have capability to adsorbed NO and NOx gases, as the CAC only has limited functional group that could removed motorcycle gases emission. Also after the chemical activation there are cristal of chemical founded on the surface of adsorbent, which resultd the reducing of pore size and other limited pore form. Ones the pores were filled with gas, then there’re only limited pores left for further adsorption. This phenomena also could be explained from the SEM analysis above (Fig.2). After the gas emission analysis using motorcycle idle position for 10 minutes, the pores were filled with dirt and other pollutant and it blocked the adsorption pathways and it made the pores become saturated. That’s why in the future reserach we suggested for modification of banana peels adsorbents with other nano particles to enhance the porosity and adsorption area of each particles produced.

There sults of this study provide an understanding of the proximate analysis and ultimate value of banana peels adsorbents produced and it suggested that the material can beused as a low-cost adsorbent for adsorbing gaseous emission and its applicable for reducing the air pollution in Banda Aceh or other Indonesian area. The RC and CAC also could be applied as one of biofilter technology along with knalpot for reducing green house gas effect from fossil fuels to the environment.

4. Conclusion
In conclusions, the proximate analysis showed that the best chemical activation temperature was using CAC H2SO4 3N 3 hours contact time for CO gas adsorption and by using CAC ZnCl2 3N 3 hour contact time for SO2 adsorption. The carbon active produced had a low moisture content, higher fixed carbon percentage and best iodine adsorption capacity. The RC and CACprepared showed best adsorption capacity on CO and SO2 gas emissions removal, but not for NO and NOx gases. The CAC has potency to be used as one of adsorbent for removing gaseous pollution or wastewater treatment.

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