Application of banana peels waste as adsorbents for the removal of CO₂, NO, NOₓ, and SO₂ gases from motorcycle emissions

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Abstract. The aims of the study were to investigate the application of banana peels as adsorbent for the removal of CO, NO, NOₓ and SO₂ gases from motorcycles emissions. The effect of different thermal activation on the characteristics of banana peels adsorbent (BPA) such as moisture content, ash content, volatile matter and fixed carbon has been studied using proximate analysis. The study of Iodine adsorption capacity of BPA was obtained at 952 mg/g adsorbent. Structure and morphology of BPA were characterized by Fourier transform infrared (FTIR) and field emission scanning electron microscopy (SEM). The results showed that BPA could significantly adsorbed the CO and SO₂ gases emissions from motorcycles, but not applicable for NO, NOₓ gases. After 10 minutes of flue gas analysis at idle mode using BPA adsorption tube, CO gas could be totally removed, from initial 19618 ppm to 0 ppm, while SO₂ gas could also be totally removed from 24523 ppm to 0 ppm. SEM test showed that temperature of activation had significant effect on the size of pores of BPA formed. BPA was suitable for application in removing CO and SO₂ gases emissions from motorcycles and it helps to reduce the green house gas effects of fossil fuel to the environment.

1. Introduction

Industrial development in the past five decades has brought the planet to a very worrying collapse from the environmental point of view because of the uncontrolled increase in the use of fossil fuels as the main energy source; the average global temperature will increase and thereby alter the ecosystem. In particular, the excess emission of gases from the internal combustion engine and industry has become one of the major causes of environmental pollution, where gases such as CO₂, CO, hydrocarbons, SO₂, and NOₓ generate volatile organic compounds (VOC) and particulate matter. These compounds have led to the greenhouse effect, acid rain, photochemical smog, stratospheric ozone depletion, and the aforementioned global warming. These events impose considerable negative effects on human and animal health due to the high toxicity of the compounds mentioned [1][2].

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Studies in a number of cities (Bangkok, Cairo, Jakarta, Santiago and Tehran, to name five) have assigned priority to controlling lead and particulate matter concentrations, which present the greatest hazard to human health. Where photochemical ozone is a problem, control of ozone precursors (nitrogen oxides and volatile organic compounds) is also important both because of the damaging effects of ozone itself and because of the secondary particulate matter formation resulting from atmospheric reactions with ozone. Carbon monoxide and toxic air contaminants have been assigned lower priority for control at the present time, but measures to reduce volatile organic compounds exhaust emissions will generally reduce carbon monoxide and toxic substances as well [3].

To reduce these emissions, several studies have used porous materials such as mesoporous materials, modified mesoporous materials, aluminas, silicon compounds, compounds derived from coal as both chemically and physically activated powders, granular materials, and fabrics modified with TiO$_2$ [4][5]. But most of it uses porous materials for UV irradius gaseous emission adsorptions modified with TiO$_2$.

Until now, there is no available literatures on the use of banana peels waste for the removal of gaseous emission from motorcycles. Only one study reported on the use of banana peels for CO$_2$ removal in the atmosphere[6]. Most of the studies were used agro-wastes for the removal of heavy metals from water and wastewater as it has a long term effects on the environment. Different adsorbents are developed from agro-wastes and used for heavy metals removal such as rice straw [7], seaweed [8], wood and bark [9], tea-waste [10], maize corn cob, jatropha oil cake, sugarcane bagasse [11], tamarind hull [12], sawdust [13], rice husk [14], saltbush [15], marine algal biomass [16], olive pomace [17], activated sludge [18], sugar beet pulp [19], wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, and charcoal [20], seafood processing waste sludge [21] and pine bark [22].

The activated carbon (AC) is a well known adsorbent that can be used efficiently for removal of a broad spectrum of pollutants from air, soil and liquids. The adsorbents are usually porous solids, and adsorption occurs mainly on the pore walls inside particles. Among them, AC is more efficient adsorbent for elimination of many pollutants (organic, inorganic, and biological) of concern in water and wastewater treatment [23]. Activated carbon (AC) is carbon material having a high porosity, high adsorption capacity, high mechanical strength, and a very large surface area. Activated carbon (AC) are widely used in industry such as to separate the various types of pollutants such as dyes and metal ions from industrial waste, as gas storage and others. Comercial ACs are generally derived from coal which is non-renewable carbon source with relatively expensive price. As an alternative, it has been extensively researched and developed ACs from biomass, such as coconut shell, palm and bamboo. [24].

In the recent study, the used of banana peels waste as the potencial adsorbent for the removal of motorcycles gas emission is important, because the public mayor concern on air pollution dispersion in Indonesia. The research to find the most efficient, low cost, environmental friendly adsorbent from agrowastes was keep on going. Banana as one of the biggest fruit commodity contributors in Aceh Province, Indonesia, in the amount of 504.850 quintals [25]. Along with the high productivity, the amount of waste from banana peels also increased. When the harvesting time, banana fruits are used only flesh while the peels is discarded to the environment. Nowadays banana peels is only used as fertilizer or as animal feed. This piles of banana peels has potency as one of raw materials for making natural activated carbon from biomass waste [26]. These wastes can be potentially used as a low-cost bioadsorbent. In addition, using these wastes in various other potential applications will eliminate them from the environment and reduce solid-waste handling, which will add some value to these wastes [27][28]. Identified functional groups of organic compounds from banana peel which act as an adsorbent were -OH, -COO, and -NH groups, which had abundant potency to be made as one of low cost biomass activated carbon through physical activation. [29].

Using environmental friendly materials for reducing gas emissions from motorcycles was our main aims. Along with this study, we hope that BPA not only could become one of alternatives most reliable adsorbent for reducing green house gas effect to the human and environment, but also could
be used in wider range of application for treating water, wastewater and gaseous pollutions in the future.

2. Experimental procedure and methodology

2.1. Preparation of Samples
Banana peels were obtained from local market in Banda Aceh, Indonesia. The peels were washed thoroughly and then cut into pieces of ± 3 cm and dried in the oven at 105 °C for 24 hour to remove the moisture content. The dried peels is carbonized at a temperature of 400 °C for 1.5 hours to become charcoal, then ground and sieved at 50 mesh. The banana peels carbon is activated thermally using a furnace at operating temperature e.i. 500 °C, 600 °C and 700 °C, respectively for 45 minutes. Banana peels activated carbon (BPA) powered then used for the characterization studies.

2.2. Chemicals
All chemicals reagents used in the titration were supplied by Merck and were of analytical grade.

2.3. Instrumentation and characterization of BPA
Proximate analysis of BPA were carried out to determine the ash percentage, and contents of moisture, volatile matter and fixed carbon. Properties of BPA particles such as Iodine absorption capacity was determined. BPA were further characterized by Fourier Tranform Infrared Spectra (FTIR) using Shimadzu IR Prestige and Scanning electron microscope (SEM) using JSM Series for morphology of BPA.

2.4. Proximate analysis
Proximate analysis of BPA was done according to standard procedure (SNI No. 06- 3730-1995)[30]. Moisture content of BPA was calculated as given in eq. (1). BPA sample was kept in a hot-air oven at 105 ± 2 °C till constant weight was obtained. Then the sample was kept in a desiccator till it reached room temperature and finally the weight of the sample was taken to determine the loss in weight due to the removal of moisture. Volatile matter was determined by heating the air dried sample of BPA in muffle furnace at 900 ± 10 °C for 7 min and calculated using eq. (2). To determine percentage ash content, the air-dried BPA sample was heated in a muffle furnace at 500 °C for 30 min; the temperature was further increased from 500 °C to 815 °C during the next 30 min and maintained until constant weight was obtained. The percentage ash was then calculated using eq. (3). Fixed carbon was obtained after deducting the sum of moisture, ash and volatile matter contents (expressed as per cent) from 100 and calculated using eq. (4). The experiment was carried out in N2 atmosphere.

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\text{% Moisture} = \frac{100 \ (\text{Loss in weight after drying})}{\text{Total weight of sample taken}}
\]  

\[
\text{% Volatile matter} = \frac{100 \ (\text{Loss in weight after heating})}{\text{Total weight of sample taken}} - \text{% Moisture}
\]  

\[
\text{% Ash} = \frac{100 \ (\text{Weight of ash obtained after heating})}{\text{Total weight of sample taken}}
\]  

\[
\text{Fixed carbon} = 100 - (\text{% Moisture} + \text{% Volatile matter} + \text{% Ash})
\]

2.5. Gasses Emission Adsorption Process
Process of gases emissions adsorption study was accomplished within 2 steps; (1) making of the adsorption tube or knalpot model for filling the adsorbents, that has been formed in cubicles size of 1x1x1 cm; (2) Gases emissions adsorption study was done on motorcycle Honda Astrea year 2000.
Measurement of CO, NO, NOx dan SO2 gases emission from motorcycle was determined using Flue gas Analyzer 6000 at idle condition, after 0, 5 and 10 minutes analysis. Removal of CO, NO, NOx dan SO2 gases emission were determined by comparing the analysis value recorded before and after adsorbents filled in the model knalpot, while the motorcycles being accelerated for 10 minutes.

3. Results and Discussion

3.1. Proximate Analysis
The results of proximate analysis on BPA prepared was shown on Table 1. The moisture content greatly affect the quality of activated carbon. The moisture content obtained ranging between 2-6%. Low water levels can be due to fewer active charcoal surface containing polar functional groups so that the interaction between polar group is small [31].

| Temperature (°C) | Moisture (%) | Volatile (%) | Ash (%) | Fixed Carbon (%) | Iodine Adsorptin (mg/gr) |
|------------------|--------------|--------------|---------|------------------|-------------------------|
| 400              | 4.00         | 14.00        | 9.00    | 73.01            | 793.19                  |
| 500              | 6.00         | 11.00        | 4.00    | 79.05            | 824.92                  |
| 600              | 2.00         | 12.00        | 2.01    | 84.03            | 951.83                  |
| 700              | 5.00         | 19.00        | 3.02    | 73.01            | 751.94                  |

The ash content is influenced by the amount of silica content, the greater the amount of silica then the resulting ash content greater. Levels of volatile substance is the result of the decomposition of substances - compilers of charcoal due to heating during the authoring process and not the composition of charcoal [31]. The results of volatile matter of activated charcoal banana peels ranges between 11-19%. Low levels of substances that evaporate due to the evaporation of the compound - non-carbon compounds that are volatile at the carbonization process.

The BPA characteristics of fixed carbon range between 73.01-84.03%. Levels of carbon bonded carbon is the fraction bound in charcoal besides fraction of water, substances evaporate and ash. High and low levels of carbon bound in charcoal influenced by the value of the ash content, content of volatile substance and hydrocarbons that are still attached to the surface of charcoal, and is also influenced by the content of cellulose and lignin materials that can be converted into a carbon atom [31].

Lower moisture content (2-9%) means that the fruits and vegetable adsorbent could be storage for longer time periods because it is resistant to mould growth. The organic nature of Fruits and vegetable adsorbents is confirmed by higher volume of volatile matter ( up to 85 %) along with raised in temperature of activation. [32] This organic matter mainly included proteins, carbohydrates and lipids, all of which are good source of nutrients. The ash content (2-9%) from fruit and vegetable adsorbents could be a good source of minerals and micronutrients.

The parameters that can precisely indicate the quality of low cost activated carbon made of banana peels biomass 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 results of analysis iodine absorption capability has ranged from 752 - 952 mg/g. Low cost carbon made of banana peels has a trend to change before and after activated, which caused by activating agent which can cause a shift based on their chemical environment. Images can be viewed on the catchment area in the position of 2850 - 2960 cm⁻¹, which contains C-H functional groups.

The processes of adsorption, which involves the transference of a solid mass in a fluid phase to the surface of a solid component, are being largely studied due to their high efficacy and for being economically viable in the treatment of wastewater effluents. The utilization of low cost material in
the production of activated carbon is an alternative pathway to food industry waste, which is usually disposed and end up losing its value [33].

3.2. Analysis of Functional Groups using FTIR (Fourier Transform Infra Red)

Figure 1 showed the comparison of the wavelength 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.

3.3 Analysis of surface morphology using SEM

The surface morphology of the BPA was analyzed using SEM (Scanning Electron Microscopy) at 1000 - 3000X. From figure 2, it could be shown that the adsorbent pores surface has more opening after being activated by thermally/physically compare to before activation process.

Figure 2 showed that before activation the BPA tend to have small pores, but after the thermal activation the pores become wider and hollower. This was mainly caused by the temperature used for carbonization, which is 400 °C. A temperature of 300°C to 400°C led to incomplete carbonization of banana peel and the cell structure is maintained. There are seemed some small pores due to the release of some volatile compounds. The study of Mendez et al. [34] showed that the main important weight
changes are produced due to the light compounds volatilization and pyrolysis transformations at 450°C. This stage is primary pyrolysis (in the 300°C to 500°C range) with evolution of most gases and tars with formation of the basic structure of the char [35].

3.4. Gas Emission Removal

The object of our research was the use of BPA as adsorbent for the removal of gaseous emission from automotive/motorcycles which has been used since year of 2000. The Motorcycle gas emission analysis was accomplished by making a model of adsorbant tube from knalpot that filled with BPA media that has formed into small cubicles shapes of 1x1x1cm. Modified shape of BPA were aims to minimize the destruction of adsorbents pores during the emission test. The BPA 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.

| Type of gas emission | Gas Emission without activated carbon (ppm) | Gas Emission adsorption using BPA media (ppm) | Adsorption efficiency (%) |
|----------------------|---------------------------------------------|-----------------------------------------------|--------------------------|
|                      | 0 min | 5 min | 10 min | 5 min | 10 min |
| CO                   | 14385 | 19618 | 10230 | 0     | 47,854 | 100   |
| NO                   | 24    | 17    | 33    | 33    | NA     | NA    |
| NOx                  | 25    | 17    | 67    | 145   | NA     | NA    |
| SO2                  | 2187  | 24523 | 13788 | 0     | 43,775 | 100   |

From Table 2, it could be explained that BPA 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 BPA adsorption tube, CO gas could be totally removed, from initial 19618 ppm to 0 ppm, while SO2 gas could also be totally removed from 24523 ppm to 0 ppm. These was caused by the total pores size of BPA particles didn’t have capability to adsorbed NO and NOx gases, as the BPA only has limited functional group that could removed motorcycle gases emission. 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.7). 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 research we suggested for modification of banana peels adsorbents with other nano particles to enhance the porosity and adsorption area of each particles produced.

The results of this study provide an understanding of the proximate analysis and ultimate value of BPA produced and it suggested that the material can be used as a low-cost adsorbent for adsorbing gaseous emission and it applicable for reducing the air pollution in Banda Aceh or other Indonesian area. The BPA 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 thermal activation temperature was at 600 °C, and 45 minute activation, as it resulting a low moisture content, higher fixed carbon percentage and best iodine adsorption capacity. The BPA prepared showed best adsorption capacity on CO and SO2 gaseous emissions removal, but not for NO and NOx gases. The BPA has potency to be used as one of low cost adsorbent for removing gaseous pollution or wastewater treatment.

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