



Mass Effect of Coconut Shell-derived Activated Carbon on Adsorption of Benzene, Toluene, Ethylbenzene, and Xylene in Motorcycle Emissions

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Abstract

The use of motorized transportation in Indonesia is now proliferating. The higher the use of motorized vehicle-based transportation in an area, the higher the potential for air pollution. One of the air pollutants is a mixture of benzene, toluene, ethylbenzene, and xylene (BTEX). This study examines the effect of coconut shell-derived activated carbon adsorbent mass which is adjusted with different thicknesses on its adsorption ability for BTEX. The adsorbent is used to adsorb the emissions of the 1990 GL-Pro motorcycle with premium fuel. The results of gas chromatography-mass spectroscopy (GC-MS) show that motor vehicle emissions contain BTEX and other hydrocarbons. ANOVA variant analysis showed that the difference in mass of activated carbon in the range of this study did not provide a significant difference in BTEX adsorption.

1. Introduction

The development of the use of motorized vehicle-based transportation in Indonesia is now overgrowing. Based on the Indonesian Central Statistics Agency (BPS), the number of motorbikes in 2019 was around 113 million [1]. The higher the use of transportation operating in an area, the higher the potential for air pollution. In-vehicle exhaust gases, BTEX compounds are often found [2]. BTEX is an organic compound that is volatile and has a relatively large solubility value in water compared to other organic compounds. This compound can spread in the environment and endanger health if it exceeds the threshold concentration. Benzene is a carcinogen that can cause leukemia [3]. Toluene, ethylbenzene, and xylene can irritate human skin and are very reactive. They are precursors for secondary air pollutants such as ozone, carbonyl, and aldehydes [4]. BTEX content in premium fuel respectively 3.15; 10.59; 2.10; 2.90% [5].

One of the adsorbents that are often used is activated carbon [6, 7, 8]. Activated carbon from coconut shells can be used as an adsorbent because it is porous, has selective

adsorption, the surface area of the mass is significant, and has a strong binding power to substances that are physically or chemically separated [9]. The substances in question are benzene gas [10], carbon monoxide [5], metal cadmium, copper, and lead [11], as well as hydrocarbons, especially BTEX [12]. There are two BTEX sampling methods in exhaust gas: passive sampling [4] and active sampling [12]. Passive sampling takes a relatively long time (about one week) compared to active sampling, which only takes 25 minutes. Both passive and active sampling use activated carbon as an adsorbent. The NIOSH standard states that the mass of activated carbon from coconut shells used for BTEX sampling is 100 mg, and 50 mg are used in one sorbent tube [12]. The mass of activated carbon is equivalent to 1.5 and 1 cm long in a sorbent tube with an inner diameter (ID) of 0.4 cm. However, studies on the effect of mass or thickness of activated carbon on the adsorption capacity of BTEX pollutants in motor vehicle emissions (gas phase) have not been reported. This research is preliminary, and the first research related to motor vehicle emission adsorption using coconut shell-based activated carbon.

2. Methodology

This research began with the manufacture of activated carbon from coconut shells. The activated carbon obtained was then applied with 3 (three) masses of activated carbon in a sorbent tube. The adsorption of exhaust pollutants from motorbikes was carried out using activated carbon in a sorbent tube. The pollutants absorbed by activated carbon were prepared and analyzed using gas chromatography-mass spectroscopy (GC-MS). The BTEX content absorbed in activated carbon was processed using the ANOVA statistical method [13].

2.1. Materials and tools

The materials used in this research were coconut shell, standard mixture BTEX 2000 mg/L (Lot. Number XA16899V) from Sigma Aldrich, n-hexane (Merck), methylene chloride (Merck - GC grade), distilled water, technical NaCl, and premium gasoline. The equipment used was glassware, micropipette, sieve, stopwatch, pump, oven, desiccator, flow meter, glass tubes with a length of 10 cm and an inner diameter (ID) of 0.4 cm, muffle furnace (Thermolyne F48000) with a capacity of 5 L and a maximum temperature of 1200°C, GC-MS from Agilent GC 7890A-MS5975C with electron ionization technique and mass analysis type that is single quadrupole. The column used was DB-5ms (5%-phenylmethylpolysiloxane) with a size of 30 m x 250 μ m x 0.25 μ m (J&W USA).

2.2. Activated Carbon Preparation

The preparation of activated carbon from coconut shell was using NaCl activator because, based on literature studies, NaCl showed the best results [10, 14, 15, 16, 17, 18]. After cleaning from the fibers, the coconut shell was heated at 350°C in the furnace for 90 minutes. The obtained carbon was then crushed until the particle size passed 80 mesh (<0.177 mm) sieve. This carbon was then activated using 10% NaCl solution for 24 hours. Next, the carbon was reheated in the furnace at 350°C for 60 minutes. The activated carbon obtained was rinsed with distilled water until a neutral pH was obtained (= 7) and again heated in an oven at 110°C for 3 hours. The activated carbon produced was then weighed for each thickness measurement 1, 1.5, and 2 cm.

2.3. BTEX Sampling

The BTEX sampling process in motorbike emissions was carried out one by one for each mass variation. Activated carbon was packaged in a sorbent tube whose ends were pre-filled with foam. After activated carbon was added, the next sorbent tube was filled with a bit of glass wool (Figure 1). This tube was then placed behind the exhausted mouth of the motorbike at a distance of 30 cm. With the aid of a rubber hose and a stative, the other end of the sorbent tube was connected to a flowmeter regulated at 0.2 L/min with the aid of a vacuum pump to draw emissions from the exhaust nozzle (Figure 2). Sampling was carried out when the engine was started idling for 25 minutes [12].

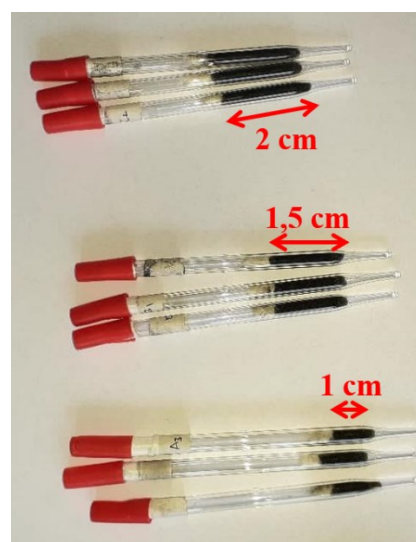


Figure 1. Activated carbon packed in sorbent tubes with different masses and thickness



Figure 2. The process of sampling adsorbent on motorbike exhaust gases

2.4. Calibration curve preparation

Calibration curves with a concentration range of 0.4 mg/L to 8.0 mg/L were prepared by diluting a standard solution of 2000 mg/L BTEX mixture with n-hexane using a measuring flask. Each standard solution made was transferred to the GC-MS vial for measurement.

2.5. Sample Preparation

The BTEX sample in the sampling adsorbent was put in a 2 mL vial extractor, added 1 mL of methylene chloride solvent, stirred with vortex, and sonicated for 5 (five) minutes at room temperature, then filtered with a PTFE filter with a pore size of 0.22 μ m. The filtrate was put into a clean vial of 1.5 mL and analyzed by GC-MS with the injector set at 250°C, split mode (ratio 5: 1) with an injection volume of 1 μ L. The oven temperature was set to 40°C for 2 minutes then gradually increased the speed of 5°C/minute to 70°C and held for 0 minutes; 20°C/minute to 280°C withheld for 0 minutes and 30°C/minute up to 299°C withheld for 3 minutes. The mass spectrometer was set with line transfer temperature at 280°C, ion source temperature 230°C, quadrupole 150°C, solvent cut 2.60 minutes, and mass scan setting 40–550 m/z, for compound identification used the data library from Willey 09 & NIST 08.

3. Results and Discussion

Coconut shell is a waste that can be processed by carbonization and activated to obtain activated carbon. In the experiment of making carbon from coconut shells, heating was carried out in stages starting from 200°C to 500°C, and a temperature of 350°C was the optimal temperature. After being activated, the activated carbon is ready to be used for the adsorption process. Adsorption is the process of collecting dissolved objects in solution between two surfaces, such as solids and gases. In this case, activated carbon is a solid which adsorbs dissolved pollutants in the gas phase [19]. The results showed that coconut shell activated carbon could adsorb hydrocarbon pollutants, especially BTEX compounds from motorcycle emissions. BTEX is a natural component in fuel, and BTEX can be present as a pollutant in vehicle exhaust emissions in the event of incomplete fuel combustion [20].

The BTEX sampling process in exhaust gas was carried out one by one for each mass variation. The sampling distance, pump pressure, time, and engine state were set. Samples that have adsorbed the flue gas content were then extracted using methylene chloride solvent and analyzed using GC-MS to identify volatile organic compounds, including BTEX compounds.

3.1. BTEX Qualitative Identification

Based on the Willey 09 & NIST 08 database on GC-MS, qualitative identification of the presence of BTEX can be seen from the retention time of each compound, which is 2,932; 4,672; 7,066 and 7,325 minutes for benzene, toluene, ethylbenzene, and xylene, respectively, as shown in Table 1.

The fragmentation base peaks of benzene (C_6H_6), toluene (C_7H_8), ethylbenzene (C_8H_{10}), and xylene (C_8H_{10}) are at m/z of 78, 92, 106, and 106, respectively. The measurement results for the BTEX standard mixture can be seen in the chromatogram profile (Figure 3). Total Ion

Chromatography (TIC) of standard mixtures of BTEX compounds showed a high peak intensity at the retention time of 2.945 minutes for benzene compounds, 4.658 minutes for toluene compounds, 7.022 minutes for ethylbenzene compounds, and xylene compounds at a retention time of 7.249 minutes. The retention time is when the peak appears after passing through the GC-MS column calculated since the sample injection. This retention time is unique for each compound. The difference in retention time of each compound is due to differences in the interaction of each compound with the column and temperature used.

Table 1. Standard data of BTEX compounds from the GC-MS library

Compound name	Retention Time (minutes)	Molecular Weight (g/mol)	Chemical Formula	Six Largest Ions (m/z)
Benzene	2.932	78	C_6H_6	78, 77, 52, 51, 50, 39
Toluene	4.672	92	C_7H_8	92, 91, 90, 65, 63, 39
Ethyl Benzene	7.066	106	C_8H_{10}	106, 91, 77, 65, 51, 39
Xylene	7.325	106	C_8H_{10}	106, 105, 91, 77, 51, 39

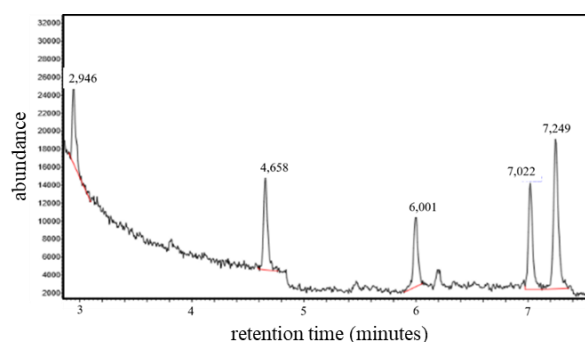


Figure 3. Chromatogram of a mixture of BTEX compounds

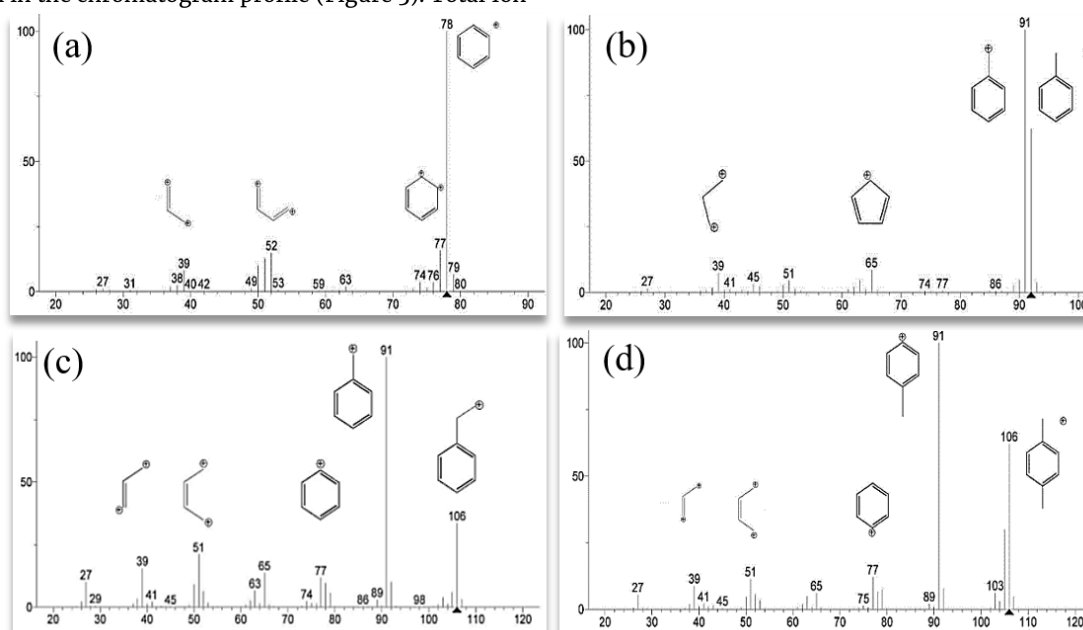


Figure 4. Fragmentation and mass interpretation of the compound (a) benzene; (b) toluene, (c) ethylbenzene; and (d) xylene

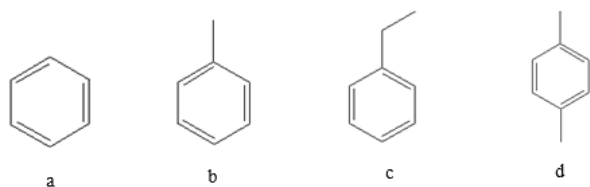


Figure 5. Structure of (a) benzene, (b) toluene, (c) ethylbenzene, and (d) xylene

The results of mass spectrometry analysis showed that the base peaks of benzene, toluene, ethylbenzene, and xylene were 78, 92, 106, and 106, respectively, as shown in Figure 1. The mass spectrum shows the mass of positive fragments (including molecular ions) relative to their concentrations. The base peak is the most abundant fragment and is stated to have a relative abundance of 100% [21]. The interpretation of mass fragmentation is used to identify chemical formulas: characteristic fragment patterns and possible fragment ions of the mass spectrum. The fragmentation patterns for BTEX compounds and their chemical formulas can be seen in Figures 4 and 5.

3.2. BTEX quantitative measurement

Figure 6 presents the standard calibration curves for benzene, toluene, ethylbenzene, and xylene, so the BTEX pollutant content in the absorbed activated carbon from motorcycle emissions is determined based on this. The correlation coefficient (R^2) value for the four BTEX calibration curves is close to the value of 1 (one). This shows a close relationship between the BTEX concentration and the peak area.

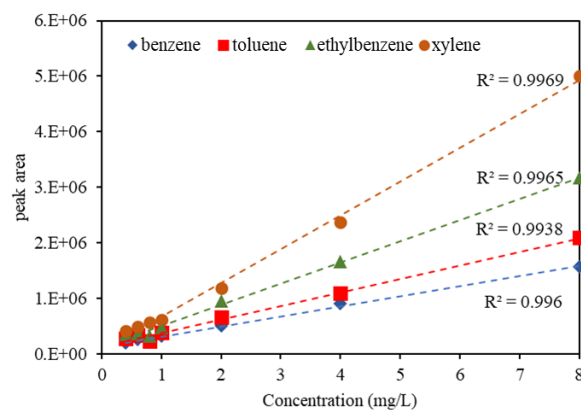


Figure 6. BTEX calibration curve

3.3. BTEX determination in exhaust gas samples

The BTEX measurement results absorbed in activated carbon from coconut shell using GC-MS are presented in Figure 7. Based on the GC-MS database presented in Table 1 and the standard BTEX retention time profile in Figure 3, the presence of BTEX pollutants in the sample chromatogram in Figure 7 can be identified: retention time of 2.922 minutes for benzene; 4,672 minutes for toluene; 7,068 minutes for ethylbenzene and xylene appeared at a retention time of 7.330 minutes.

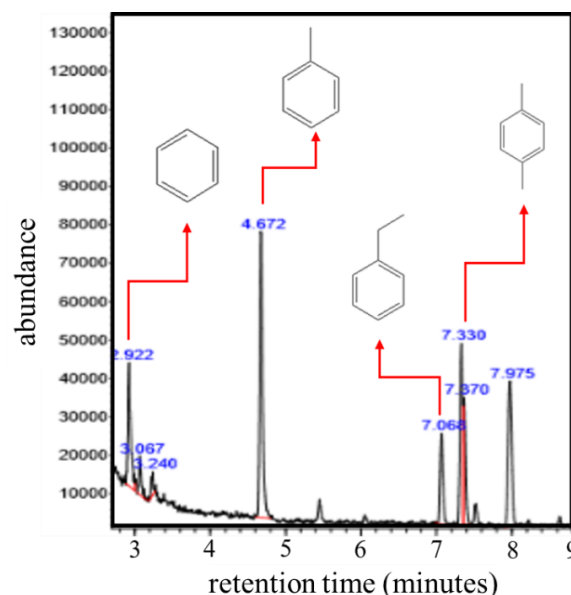


Figure 7. Chromatogram of the sample

3.4. The effect of the different mass of activated carbon on contaminant uptake

Three mass variations of activated carbon are equivalent to the thickness of activated carbon 1, 1.5, and 2 cm active when sampling pollutants. The masses are about 50 each, 100; and 160 mg. Each treatment was made 3 (three) times repetition. The average BTEX content of the experimental results and their ranges are presented in Figure 8.

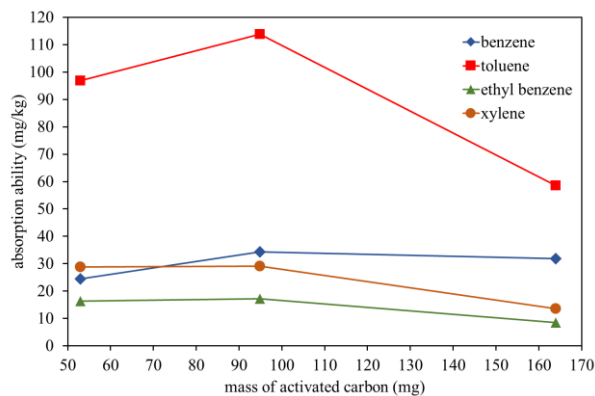


Figure 8. The relationship between the mass of activated carbon and adsorption ability (n = 3)

The adsorption process occurs as the mass of activated carbon increases. This shows that the adsorbent mass affects the adsorption process. As the mass of the adsorbent increases, the adsorbed value increases. The adsorption process is stated to stop when the adsorbent mass has reached its saturation point (it reaches an equilibrium condition) if the surface has been filled with an adsorbate. The adsorption process is no longer effective [22]. Based on the graph of the mass relationship of activated carbon to the BTEX content in Figure 8, all curve profiles show that the adsorption process increases with the increasing mass of activated carbon. The adsorption process showed its highest point at a mass of 94.85 (equivalent to (100) mg in the NIOSH standard).

Table 2. ANOVA list

SV	df	Benzene				Toluene				Ethyl benzene				Xylene			
		SS	MS	F _{ratio}	F _{table}	SS	MS	F _{ratio}	F _{table}	SS	MS	F _{ratio}	F _{table}	SS	MS	F _{ratio}	F _{table}
Mean	1	8216.96	8216.96			72531.07	72531.07			1760.36	1760.36			5096.73	5096.73		
Mass	2	157.81	78.90	0.51	5.14	4812.07	2406.04	1.79	5.14	133.69	66.84	1.70	5.14	475.03	237.52	2.88	5.14
Error	6	932.25	155.38			8078.38	1346.40			235.44	39.24			494.50	82.42		
Total	9	9307.02				85421.52				2129.49				6066.26			

Noted: SV = Source of Variation; df = degree of freedom; SS = Sum of Squares; MS = Mean Square

After that, the absorbed BTEX concentration decreased at a mass of 164 mg (equivalent to 160 mg in the NIOSH standard). The concentration range at the optimum mass shows a relatively large concentration range compared to the other two masses. This happened because several factors such as air temperature, humidity, and wind direction during the sampling were not used as control variables. By considering the immense error value in Figure 8, the ANOVA test was carried out to determine how much influence mass had on the adsorption ability of BTEX.

Based on the results of the ANOVA calculation, it is known that mass does not have a significant effect on BTEX absorption. The results of data processing using ANOVA in Table 2 show that the mass treatment of activated carbon has no effect on the adsorption power of activated carbon on BTEX. The F_{ratio} value obtained by BTEX is 0.51 consecutive; 1.79; 1.70 and 2.88 are smaller than F_{table} ($df_1 = 2$; $df_2 = 6$ & $\alpha = 0.05$) = 5.14. Based on the ANOVA calculation results, further analysis of the isotherm/adsorption equilibrium mechanism cannot be carried out.

The content of ethylbenzene and xylene compounds from flue gas which is absorbed by activated carbon from coconut shells is still classified as normal, but on the contrary, for benzene and toluene compounds. The highest ethylbenzene concentrations (17.14 mg/kg) and xylene (29.10 mg/kg) were lower than the threshold value of Permenakertrans No.13/MEN/X/2011, which are 50 and 100 ppm, respectively, for ethylbenzene and xylene. Meanwhile, the highest experimental concentrations for benzene (34.3 mg/kg) and toluene (113.84 mg/kg) were relatively higher than the threshold values of 0.5 ppm for benzene and 100 ppm for toluene. This is caused by incomplete combustion.

4. Conclusion

Based on ANOVA analysis, the differences in mass of activated carbon in the study ranges were 50, 100, and 160 mg with a thickness of 1; 1.5; and 2 cm did not give a significant difference in the adsorption power of activated carbon against BTEX compounds in motor vehicle emissions.

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