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Effect of TiO_2 on Orange Peel Activated Carbon Composite in Reducing Carbon Monoxide and Hydrocarbon Gas Emissions

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ABSTRACT

The transportation sector is a contributor to CO and HC gas emissions. This study aims to see the effect of adding TiO_2 on activated carbon as a material for reducing CO and HC gas emissions. Activated carbon (AC) was synthesized from orange peel waste at a carbonization temperature of 600℃ with a 10% (w/v) $ZnCl_2$ activator. Composite AC/TiO_2 was prepared by a simple mixing method. This process obtained TiO_2-modified activated carbon material with variations in TiO_2 concentrations of 0%, 10%, 15%, 20%, and 25%. Scanning Electron Microscope (SEM) was performed to obtain information on the AC/TiO_2 surface morphology. In the application as a CO and HC gas emission reduction material, the results of mixing AC/TiO_2 are mixed with a 10% (w/v) solution of Polyvinyl Alcohol (PVA) as an adhesive and molded in the shape of a filter with two variations hole sizes with a diameter of 1 cm and 0.3 cm. Composite filter performance tests were carried out using a gas analyzer. The best result for reducing gas emissions occurred at a concentration of TiO_2 15% with reduction power to reduce CO gas emission up to 53.79% and HC gas emission up to 55.57%.

1. INTRODUCTION

In Indonesia, the surge in motor vehicles parallels population growth, with the Central Statistics Agency indicating a 1.88% rise in motorization from 2019 to 2020, a trend predicted to continue. This upswing contributes to air pollution, with gasoline engines emitting carbon monoxide (CO) and hydrocarbons (HC)—byproducts of incomplete combustion known to trigger eye irritation, asthma, and even cancer (Ogur & Kariuki, 2014).

Activated carbon is a prominent tool in curbing air pollution. Its non-toxic, adaptable, and effective nature renders it an outstanding absorbent (Bansal & Goyal, 2015). Research has delved into producing activated carbon from various organic wastes, utilizing durian peels to capture CO and HC (Yuliusman et al., 2020), banana peels for CO, NOx, and SO2 (Viena et al., 2018), coconut shells for CO, HC, and CO2 (Winoko & Wicaksono, 2021), and coffee shells for CO and NOx (Redha et al., 2018). Orange peels, rich in lignocellulose with cellulose at 69.1%, hemicellulose at 5.4%, and lignin at 19.8% (Ayala et al., 2021), emerge as a promising precursor. Their high lignocellulosic content is crucial for producing activated carbon with adequate surface area and thermal stability. Furthermore, this renewable biomass offers an ecological and economic advantage over non-renewable sources like coal (Ibeh et al., 2019; Neme et al., 2022).

Incorporating TiO2 as a catalyst enhances the surface area and efficacy of biomass-derived activated carbon in mitigating vehicular emissions due to its expansive surface and stability within mesoporous structures (Dey & Mehta, 2020). Notably, TiO2-enhanced low-density polyethylene (LDPE) activated carbon has shown remarkable efficiency, reducing CO by up to 74.83% and HC by up to 67.10% (Yuliusman et al., 2019). Additionally, activated carbon with TiO2 has been documented to significantly decrease CO, NO2, HC, and SO2 emissions (Basuki, 2007a; Basuki, 2007b).

Departing from these precedents, our research will synthesize activated carbon from orange peel waste, incorporating TiO2 using a straightforward mixing method. We will employ Scanning Electron Microscopy (SEM) to examine the surface morphology of the AC/TiO2 composite. Its efficiency in curbing gas emissions will be assessed using a gas analyzer. Innovatively, we bind the AC/TiO2 composite with Polyvinyl Alcohol (PVA) to create a matrix, and the study will focus on quantifying the reduction of CO and HC emissions in motorcycles.

2. METHOD

2.1 Tools and Materials

The tools used in this research were a 100-mesh sieve, furnace, gas analyzer, grinder, filter paper, mixer, oven, pH meter, PVC pipe, and scales. The materials used in this study were distilled water, Siam orange peel, granular PVA, TiO_2 (anatase phase), and $ZnCl_2$.

2.2 Synthesis of Activated Carbon (AC)

The synthesis process begins with cleaning and washing the collected orange peel. After that, orange peels were dried under sunlight for 6 hours. The dried orange peel was carbonized using a furnace at a temperature of 600℃ with a 1-hour holding time and then crushed and sieved with a size of 100 mesh (Kristianto & Arie, 2015). After that, we used $ZnCl_2$ with a concentration of 10% (weight to volume (w/v)) and a ratio of charcoal and $ZnCl_2$ is 1:2 to activate the carbon chemically. After 24 hours, activated carbon was washed using distilled water until the pH of the washing was neutral (pH = 7) to remove carbonized impurities. The activated carbon was then dried using the oven at a temperature of 150℃ for 3 hours (Erprihana & Hartanto, 2014). The yield of carbonization and activated carbon was determined using Equation (1):

$$\text{Yield (\%)} = \frac{m_\text{f}}{m_\text{i}} \times 100 \tag{1}$$

where m_f is the final mass in g unit, and m_i is the initial mass in g unit.

2.3 Fabrication of Composite Filter

The activated carbon was then mixed with TiO_2 using a mixer for 30 minutes (Dirga et al., 2011). We varied the TiO_2 added to activated carbon with 0%, 5%, 15%, 20%, and 25%, as seen in Table 1.

Table 1 Composition of the composite filter.

Materials	Mass fraction (g)				
	C_1	C_2	C_3	C_4	C_5
Activated carbon	25	25	25	25	25
Titanium dioxide	0	2.5	3.75	5	6.25
Polyvinyl alcohol	2.5	2.5	2.5	2.5	2.5

A molded-composite filter was produced using a 10% (w/v) polyvinyl alcohol (PVA) solution, prepared by dissolving 2.5 grams of granular PVA in 25 ml of distilled water. The PVA solution was utilized as a matrix for the incorporation of a mixture of activated carbon (AC) and titanium dioxide (TiO_2). The resulting mixture was molded into a thickness of 3 cm to form the interior part of a reactor constructed from a 5.5 cm diameter PVC pipe. The molded-composite filter was fabricated with two variations of hole diameters, measuring 1 cm and 0.3 cm, respectively. Subsequently, the filter was dried at 120℃ (Basuki, 2007a).

2.4 Experimental Setup

To evaluate the efficacy of the molded-composite filter in reducing carbon monoxide (CO) and hydrocarbon (HC) gas emissions, a gas analyzer from the UPT PKB Pontianak Transportation Agency was employed. The study focused on two-wheel motor vehicles manufactured in 2015. The experimental procedure involved preheating the motor vehicles under idle conditions for 5 minutes, then connecting the PVC pipe reactor to the motor exhaust. A probe from the gas analyzer was inserted into the reactor to measure the gas emissions. Control parameters were obtained by conducting tests without the composite filters, after which variations of the composite filters were introduced. The first sample had a hole diameter of 1 cm, and the subsequent one had a diameter of 0.3 cm, with varying concentrations of TiO_2 ranging from 0 to 25%. The testing duration was set at 5 minutes for each test, and data were recorded at 30-second intervals. Figure 1 shows the schematic from the experimental setup.

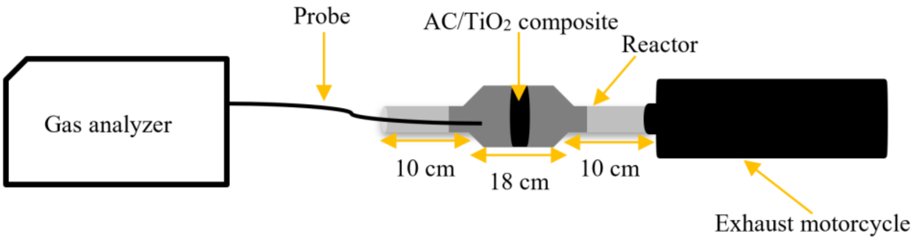


Figure 1 Experimental schematic.

Following the completion of all tests, the reduction efficiency of the composite filter in reducing CO and HC gas emissions were calculated using Equation (2). where G_0 is a gas emission without composite filter (% or ppm), and G_n is a gas emission with the composite filter (% or ppm).

$$\text{Reduction Effieciency } (\%) = \frac{(G_0 - G_\mathrm{n})}{G_0} \times 100 \tag{2}$$

3. RESULTS AND DISCUSSION

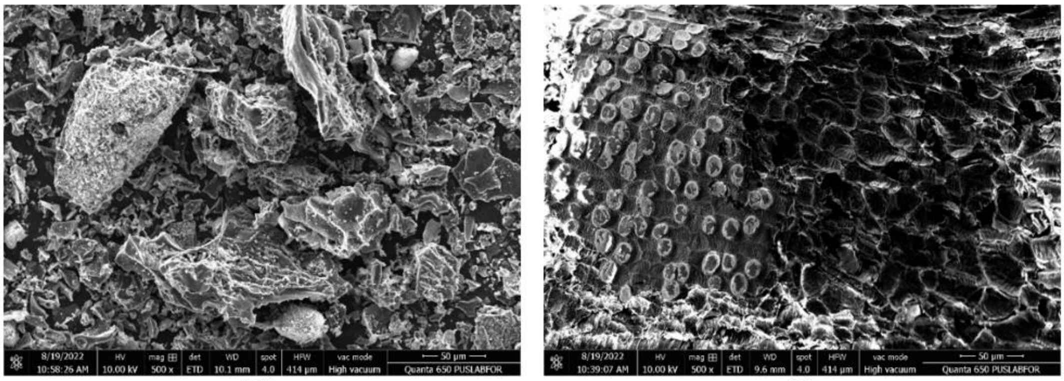
3.1 Synthesis and Characterization of Orange Peel Activated Carbon

The orange peel resulted from dehydration and carbonization stages of synthesizing activated carbon, are seen in Figure 2(a) and (b). In Figure 2(a), the orange peel was dried under sunlight until it was completely dry. Next, the orange peel was chopped into small pieces to optimize combustion during the carbonization process, as shown in Figure 2(b). The resulting charcoal (carbon) was black, indicating an increase in carbon compounds resulting from the decomposition of lignocellulosic compounds present in the orange peel. Although a carbonization temperature of 600℃ can produce perfect charcoal, it also increases combustion residues, resulting in a lot of ash. The average mass of orange peel carbon at 600℃ was only 23.43%, as the weight loss process occurs below 600℃ due to the dehydration process and the release of volatiles from the cellulose structure in the orange peel (El Nemr et al., 2020). Higher carbonization temperatures and longer holding times can decrease the yield of carbonization due to the release of volatile matter in the orange peel (El Nemr et al., 2021). The amount of volatile matter released on the orange peel through high temperatures is the cause of the decrease in the yield of carbonization. In Figure 2(c), the resulting carbon from the carbonization process was ground into a powder using a grinder to obtain smaller particle sizes ($\geq 150\ \mu$) to increase the surface area. The surface area of carbon is defined as the ratio of the total surface area to its mass, with smaller particle sizes resulting in greater surface area (Wahyuni et al., 2022). The activated carbon was then produced through the activation process with the $ZnCl_2$ compound, resulting in a gain of 88.1% in the activation process.

(a) (b) (c)

Figure 2 Results of (a) dehydration step (b) carbonization step, and (c) activated Carbon.

The surface morphology of the carbonization and activation stages is illustrated in Figure 3. The synthesis of activated carbon at a carbonization temperature of 600°C showed significant impurities in the carbon before activation. Figure 3(a) demonstrates the presence of impurities that could contaminate and clog the carbon pores. The dehydration reaction and decomposition of lignocellulosic materials determine the carbonization process. The conversion of these materials into carbon at high temperatures involves the release of H_2O, CO, CO_2, CH_4, and tar, which become impurities in the carbonization product (El Nemr et al., 2021). Cleaning the surface area requires chemical activation to remove the impurities trapped in the carbon pores and increase the adsorption capacity (Erprihana & Hartanto, 2014). Generally, the chemical activation process using the $ZnCl_2$ compound can open the pores of the activated carbon and clean its surface area (Figure 3(b)). Using the $ZnCl_2$ activator can break hydrocarbon bonds and expand the surface pores of activated carbon, enhancing the adsorption process (Cipto et al., 2021). However, in Figure 3(b), some parts of the pores remain unopened due to the lack of physical activation, which can assist in increasing the surface area of the activated carbon.



(a) (b)

Figure 3 SEM characterization with 500× magnification (a) charcoal and (b) activated Carbon.

3.2 Composite Filter

The composite filters developed and investigated in this study are shown in Figure 4. The composite filters are designed in a cylindrical shape with a hollow interior. This hollow cylinder configuration is intended to facilitate the proper circulation of exhaust emissions from motorized vehicles through the reactor, thereby enhancing filtration efficiency (Widihati et al., 2021). As depicted in Figure 4, the increase in the concentration of TiO_2 impregnation onto the activated carbon results in a grayish coloration of the composite filter. This is attributed to the inherent whiteness of TiO_2, which affects the color of the activated carbon.

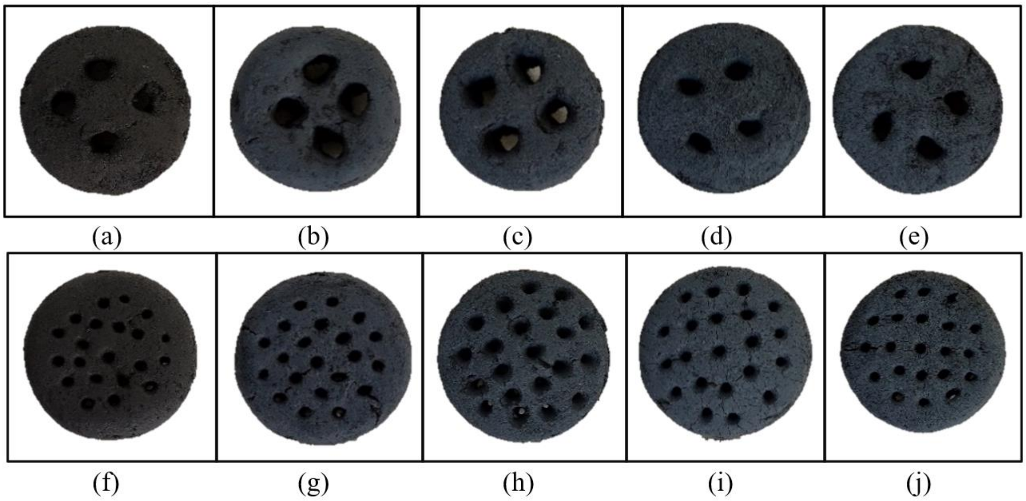
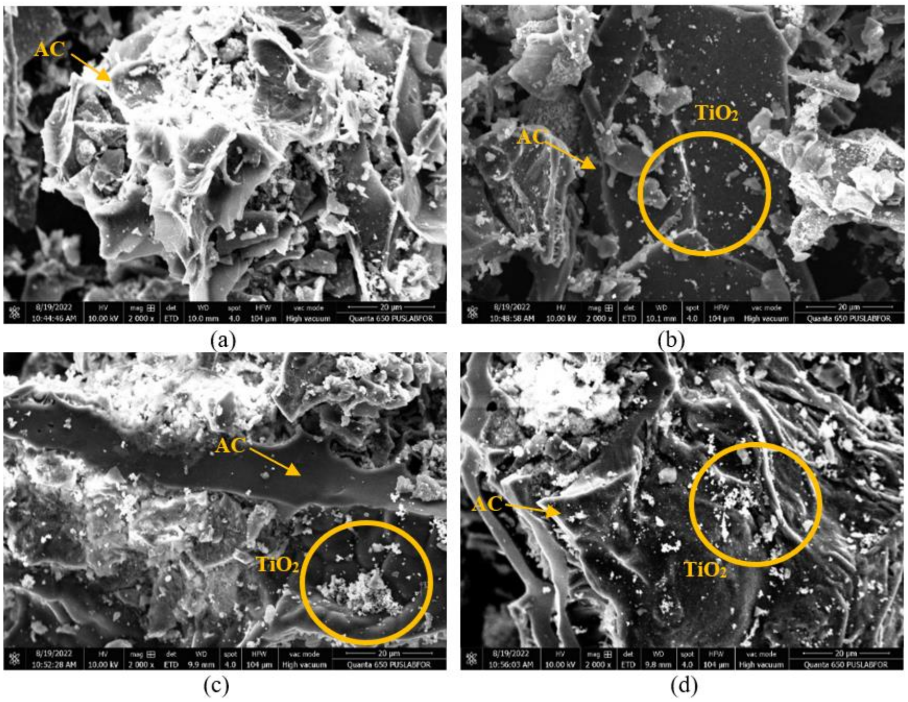

(a) (b) (c) (d) (e)
(f) (g) (h) (i) (j)

Figure 4 The configuration of the composite filter with holes of 1 cm in diameter and TiO_2 concentration of (a) 0 %, (b)10%, (c) 15%, (d) 20%, (e) 25%, and with holes of 0,3 cm in diameter and TiO_2 concentration (f) 0 %, (g)10%, (h) 15%, (i) 20%, (j) 25%.

3.3 Surface morphology of AC/TiO_2

The surface morphology of the composite AC/TiO_2 is examined using SEM images. Figure 5 shows the images of the activated carbon particles and the distribution of TiO_2 on the activated carbon. The characteristics of TiO_2 particle distribution differ for each concentration. TiO_2 particles at a 10% concentration are not clearly visible due to the small amount applied. At higher concentrations (Figures 5(b)-(d)), the TiO_2 particles are visible on the surface of the activated carbon, where they tend to overlap with one another, forming irregular white lumps of non-uniform size (Septiani et al., 2015). This overlapping phenomenon may lead to the poor catalytic performance of the TiO_2 catalyst, as the activity of heterogeneous catalysts typically depends on the surface area of the particles. Consequently, the catalytic process may become less efficient.

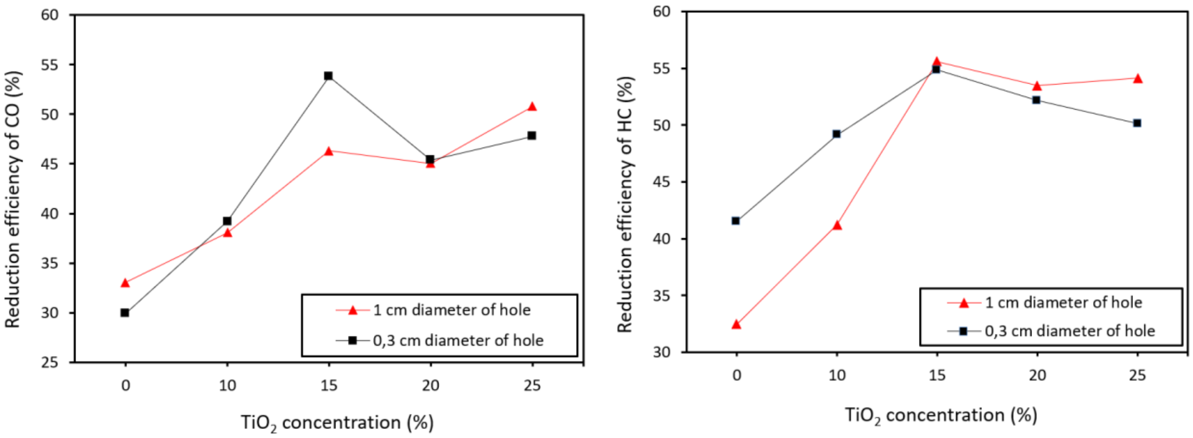


(a) (b)
(c) (d)

Figure 5 SEM characterization with 2000× magnification of AC/TiO_2 with concentration (a) 10%, (b) 15%, (c) 20%, (d) 25%.

3.4 Reduction of CO and HC gas emissions

The relationship between the concentration of TiO_2 and the reduction efficiency of CO and HC gas emissions is presented in Figure 6. Figures 6(a) and 6(b) illustrate that the most effective reduction of CO and HC gas emissions occurs at a concentration of 15% TiO_2. The good performance of 15% TiO_2 in reducing CO and HC emissions is attributed to the optimal distribution of TiO_2 on the activated carbon surface, as evidenced in Figure 5(b).



(a) (b)

Figure 6 Relationship between TiO_2 concentration and reduction power (a) CO and (b) HC.

The reduction of CO and HC gases is attributed to the presence of pores in the activated carbon, which are capable of adsorbing gas emissions, as well as the role of TiO_2 as a catalyst agent that oxidizes CO and HC gas emissions into environmentally friendly compounds. The oxidation reaction by the TiO_2 catalyst for CO gas emission follows the reaction (Setiyono & Widjanarko, 2018) :

$$2CO + O_2 \rightarrow 2CO_2,$$

while HC gas emission follows the following reaction:

$$HC + O_2 \rightarrow CO_2 + H_2O.$$

CO and HC gases are oxidized to CO_2 and H_2O due to the good performance of TiO_2 on the activated carbon surface. The impact of varying hole diameters on the composite filter was found to be insignificant in reducing CO gas emissions, unless for 15% TiO_2 concentrations. The addition of TiO_2 at higher concentrations tends to decrease the reduction efficiency. This might be because the TiO_2 particles do not work optimally due to overlapping on specific areas of the activated carbon surface. However, there was an anomaly at 25% of TiO_2, the efficiency is slightly higher than the 15% for CO reduction. We do not know precisely the reason of which this phenomenon occurred. However, we suspected that the pore structure of activated carbon also plays a role in CO adsorption at 25% (Wang et al., 2022). On the other hand, the 0.3 cm-diameters of filter holes has a higher HC gas reduction efficiency for concentrations of TiO_2 below 15%. As in CO gas reduction, the efficiency of HC reduction is also optimum at a 15% concentration of TiO_2. While applying the filter composites varies the amount of gas adsorbed, the modification of activated carbon by adding TiO_2 catalyst clearly gives a significant effect for pollutant gases adsorption, with an increase of reduction efficiency of about 25% for both gases.

3.5 Comparison material

To see the containment effect of the composite filter, we also conducted a test using plasticine with a diameter and width similar to that of the composite filter. Plasticine was chosen because it has no pores and has a high density, so it is believed that there will be no absorbed gas emissions. Table 2 shows that plasticine did not reduce CO and HC gas emissions. Thus, it can be said that the composite filter has no containment effect on CO and HC gases because it will reduce all the gas that passes in the reactor. We also calculated the standard deviation (SD) to obtain the data distribution. The results of the standard deviation of CO and HC gas emissions still occur in the range of 20% of the average data, which indicates that they are still in a good range for the average value obtained.

Table 2 Concentration of gas emissions through plasticine filter

Type of gas	Initial gas	Final gas	
		1 cm diameter of hole	0.3 cm diameter of hole
CO (%)	0.23 ± 0.01	0.24 ± 0.01	0.23 ± 0.01
HC (ppm)	103.6 ± 15.89	104.4 ± 14.71	107.7 ± 17.36

4. CONCLUSION

The synthesis of activated carbon from orange peel has been successfully achieved, indicating its promising potential as a substrate for adsorbents aimed at curtailing gaseous pollutants. The incorporation of TiO_2 as a catalyst into the activated carbon matrix has demonstrated an enhanced reduction in both CO and HC emissions. Nonetheless, it was observed that excessive TiO_2 can detrimentally affect the adsorption capabilities, potentially due to the agglomeration of TiO_2 on the activated carbon surface, which underscores the need for optimal catalyst loading. Moreover, the study found that the pore diameter of the activated carbon did not significantly impact the reduction of CO and HC gases. The application of the AC/TiO_2 composite led to a reduction in CO emissions by up to 53.79% and HC emissions by up to 55.57%, illustrating its effectiveness in mitigating vehicular pollution.

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