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# EFFECT OF PALM OIL FIBER-TiO<sub>2</sub> RATIO IN THE COMPOSITE ON THE REDUCTION OF BTX AND FORMALDEHYDE IN THE AIR

(Kesan Nisbah Serat Kelapa Sawit-TiO<sub>2</sub> dalam Komposit bagi Pengurangan Kandungan BTX dan Formaldehid di Udara)

Nor Rahafza Abdul Manap<sup>1</sup>, Roslinda Shamsudin<sup>1</sup>\*, Mohd Norhafsam Maghpor<sup>2</sup>, Muhammad Azmi Abdul Hamid<sup>1</sup>, Azman Jalar<sup>1</sup>

<sup>1</sup>School of Applied Physics, Faculty of Science and Technology Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia <sup>2</sup>National Institute of Occupational Safety and Health Lot 1, Jalan 15/1, Seksyen 15, 46500 Bandar Baru Bangi, Selangor, Malaysia

\*Corresponding author: linda@ukm.edu.my

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## Abstract

The effect of palm oil fiber-TiO<sub>2</sub> ratio in the composite on the reduction of benzene, toluene, xylene and formaldehyde in the air is studied. The ratio was set at 1:0, 1:9 and 5:5. The combination of adsorption process by palm oil fiber and photooxidation of volatile organic compounds by titanium dioxide was revealed. The composite were prepared by using mechanical milling technique. The performance of the composite was characterized in terms of percentage of recovery of benzene, toluene and xylene (BTX) using GC/FID and formaldehyde concentration reduction using formaldehyde meter. The results of recovery of the BTX by palm oil fiber/titanium dioxide composite were more than 90%. The palm oil fiber/titanium dioxide composite has successfully reduced the concentration of formaldehyde by up to 66.7%. Therefore, the palm oil mesocarp fiber/titanium dioxide composite produced is able to reduce the concentration of volatile organic compounds.

Keywords: mesocarp fiber, palm oil fiber, titanium dioxide, photocatalyst, photo oxidation, volatile organic compunds

## Abstrak

Kesan nisbah serat kelapa sawit-titanium dioksida dalam komposit bagi pengurangan kandungan BTX dan formaldihid dalam udara telah dikaji. Nisbah telah ditetapkan sebagai 1:0, 1:9 dan 5:5. Kombinasi proses penjerapan oleh serat kelapa sawit dan proses oksidasi cahaya sebatian organik meruap oleh titanium dioksida telah dijelaskan. Serbuk komposit serat kelapa sawit-titanium dioksida telah disediakan menggunakan kaedah kisaran mekanikal untuk mendapatkan serbuk komposit. Prestasi komposit telah diuji dari segi nilai peratusan ujian pemulihan benzena, toluena dan xilena (BTX) menggunakan kromatografi gas dengan pengesan pengionan api (GC/FID) dan peratusan pengurangan kepekatan formaldehid menggunakan meter formaldehid. Nilai peratusan ujian pemulihan BTX yang diberikan oleh serbuk komposit melebihi 90%. Serbuk komposit dari serat kelapa sawit dan titanium dioksida telah berjaya mengurangkan kepekatan formaldehid sebanyak 66.7%. Oleh itu, komposit yang dihasilkan dari serat kelapa sawit dan TiO<sub>2</sub> boleh mengurangkan kepekatan sebatian organic meruap dalam udara.

Kata kunci: serat mesokap kelapa sawit, serat kelapa sawit, titanium dioksida, pemangkin cahaya, sebatian organik meruap

## Introduction

Indoor air pollution can contribute to many health issues such as headache, dizziness, irritation, cancer and respiratory difficulties [1-4]. The common volatile organic compounds (VOCs) that usually exist in indoor air or a

building are benzene, toluene, isomeric xylene and formaldehyde. These pollutants were from different sources such as incomplete combustion of by-product, construction materials and exhaust emission [2, 5]. In addition to the nature of a new or old building that utilized furniture, paint, adhesive sealants, building materials and floor panels that are recognized as the source of these VOCs [6].

VOCs which can cause various side effects can be trapped and reduced by using adsorbent materials. There are numbers of adsorbent that has been used to treat air pollutants. Local raw minerals such as aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), silicon dioxide (SiO<sub>2</sub>) and titanium dioxide (TiO<sub>2</sub>) had been used to remove dimethyl benzene, one of the volatile organic compounds [7]. Whereas nanosilica was used to remove formaldehyde from polluted air [8].

Traditionally, the air pollutants were reduced by increasing the air exchange and controlling the pollutant sources [9]. Recently, photocatalytic oxidation process has been used to remove trace-level organic contaminants in air and has received considerable attention because this technology can be potentially applied in office buildings, factories, labs, homes and cars [10]. TiO<sub>2</sub> is a well-known decomposing agent that has high photo stability, commercial availability, low cost and relatively good activity that uses photocatalytic oxidation process to degrade organic pollutants [11]. In this study, palm oil fiber/TiO<sub>2</sub> composite with different ratio are fabricated to act as adsorbing material using passive sampling technique. The result of percentage of recovery of the prepared composite was compared with the standard percentage value set by National Institute of Occupational Safety and Health (NIOSH). The effect of photocatalyst activity by adding TiO<sub>2</sub> to palm oil fiber was discussed in terms of formaldehyde concentration reduction percentage.

## Materials and Methods

Titanium (IV) oxide powder (99.8 % trace metal basis) from Sigma Aldrich, the standard solution of benzene, toluene, pm-xylene and o-xylene were analytical grade with >99% purity, brand Dr Ehrenstorfer. Carbon disulfide with  $\leq 0.001\%$  benzene was purchased from MERCK. Commercial activated charcoal made from coconut shell was purchased from SKC, 1.8 ml glass vial with PTFE lined caps were purchased from Agilent for gas chromatography analysis.

## Preparation of composite powder material

Palm oil fibers were washed with distilled water to remove dirt and contaminants. It was dried in the oven at  $105\,^{\circ}$ C for 24 hours. Then the palm oil fibers were undergo a series of grinding process; started with grinder (Model, Rocklab grinder TC 40) for 10 minutes and were sieved using rotary sieve (38 micron). It was then ball milled at 600 rpm for 30 minutes. TiO<sub>2</sub> powder together with the palm oil fiber mixture was ball milled at 600 rpm for 30 minutes. Samples were labelled as POFN for 100% palm oil fiber, R1 for 10% titanium dioxide and R5 for 50% titanium dioxide.

## Preparation of stock and standard solution

Stock standard solution of toluene, pm-xylene and o-xylene were prepared by adding 1 ml of each standard into 25 ml volumetric flask. Stock standard solution of benzene was done by adding 0.1 ml of standard benzene to 20 ml volumetric flask. Stock solution of formaldehyde was prepared by adding 50 mg of formaldehyde into 100 ml volumetric flask. Then, 5 ml of the stock solution was taken and added into 100 ml volumetric flask to prepare formaldehyde standard solution of 10 ppm.

## **Recovery test**

Carbon disulfide was added into each stock solution to make it either 25 ml or 20 ml solution. Different concentration of standard solution i.e. 8 ppm, 10 ppm and 12 ppm were prepared from stock standard solution. Standard calibration curves for each parameter are performed in Chemstation as stated in instrument manual. 150 mg sample powders with particle size ranges from 47nm to 94.8 nm for palm oil fiber and 62 nm to 111 nm for titanium dioxide were placed in screw cap glass vials and spiked with known amount of benzene, toluene, pm-xylene and o-xylene (BTX) from the standard solution and left in a refrigerator at 4°C for 24 hours. 1 ml carbon disulfide was added to each vial and immediately closed up. The vials were agitated for 30 minutes and then analysed using gas chromatography with flame ionization detector. A bar chart of recovery percentage was drawn

for comparison purposes. The percentage of recovery was calculated by dividing recovered value with spiked value times by 100.

## Formaldehyde test

Stock standard solution and a standard solution of formaldehyde were prepared as above. The formaldehyde solution was heated on a hotplate at 50  $^{\circ}$ C. 10 ml of the standard solution was pipetted into a petri dish and placed inside a 457 x 305 x 305 mm test chamber. The test chamber with 55% relative humidity was set up with a 220-240 V  $\sim$  50/60 Hz 27 Watt lamps. The concentration of formaldehyde was measured by MultiRAE Lite formaldehyde meter. The composite sample was placed inside the test chamber when the formaldehyde meter gave 1 ppm reading on the screen. The light intensity and relative humidity in test chamber maintained as constant.

### **Results and Discussion**

Volatile organic compounds used in this study were toluene, and xylene with three isomers; ortho-, meta-, parasubstitution. A good sorbent should be able to desorb all the absorbed analytes [12]. Figure 1 shows that the composite adsorbed all the hazardous VOCs because the obtained value of the percentage of recovery more than 100%. The percentage of recovery for palm oil fiber/titanium dioxide composite powder was calculated using Equation 1 which is given by the area under peak of chromatogram. The amount recovered is the value given by area under peak by gas chromatography as expressed in equation 1 below.

Percentage of recovery = (amount recovered/amount spiked) 
$$\times 100$$
 (1)

As shown in Figure 1(a - c) sample with 100 %, 90 % and 50 % palm oil fiber have more than 100 % recovery of toluene, pm-xylene and o-xylene. For composite powder that was spiked with 8 ppm and 10 ppm of selected analytes, the percentage of recovery ranges from 97 % to 121 %. The increasing number of analytes available that react with the chemical structure and functional group of palm oil fiber gave the highest percentage of recovery, i.e. 203 %. It was found that, the percentage of recovery is very much depending on the heating rate, the gas flow rate and purging time of the gas chromatography [13]. In this study the optimum heating rate and gas flow rate for maximum percentage of recovery was 10 ml/min and 2.0 ml/min, respectively. This finding is in agreement with result studied by Thammakhet and Muneesawang [13] where the optimum heating rate is needed to provide a high percentage of recovery without lowering the adsorption performance of the adsorbent and minimizes the analytes loss. Another possible reason for this observation is contributed by carbon disulfide. Carbon disulfide was used as eluent to elute the compound during the early stage of recovery analysis. When the gaps between double-bonded carbon atoms are similar or greater than Van der Waals separation, direct benzene-benzene polymerization is expected to occur. Due to the carbon disulfide assisted polymerization of the benzene ring in toluene and xylene, high percentage of recovery is obtained similar as reported by Ciabini et al. [14]. In Malaysia, the National Institute of Occupational Safety and Health has set a standard percentage of recovery value. All the adsorbent must meet the 75 % recovery criteria. Result below than 75 % is not accepted.

From the results of recovery for each of the analyte concentration, the palm oil fiber used was able to capture the hazardous volatile organic compounds. All the samples gave a value that exceeds the standard requirement set by NIOSH. The effect of TiO<sub>2</sub> added into the palm oil fiber in term of the formaldehyde reduction is shown in Figure 2. POFN, R1 and R5 samples have successfully reduced the formaldehyde concentration by 62 %, 63 % and 67 % respectively. Photocatalytic degradation by TiO<sub>2</sub> has contributes to better pollutant reducer property of the palm oil fiber composite powder. TiO<sub>2</sub> act as absorbent that absorbed a photon containing energy when it was irradiated by light. The energy that equal or larger than the band gap caused the electron to be excited from the valence band to a conduction band which created vacancy in the valence band. In this reaction, electron hole pair namely, h<sup>+</sup> and e<sup>-</sup> are powerful oxidizing and reducing agents respectively [21]. Therefore, formaldehyde is oxidized to carbon dioxide and water according to Equation 2. As report by [15], formaldehyde decomposition rate is depends on humidity, UV light intensity and amount of photocatalyst. Other factors that affecting photocatalytic degradation are adsorption properties and photocatalytic activity of the catalysts [16].

$$HCHO + O_2 \rightarrow CO_2 + H_2O \tag{2}$$

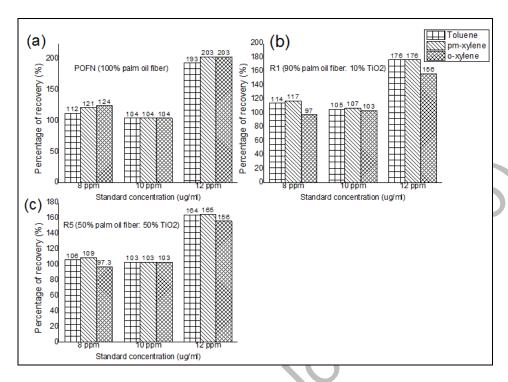


Figure 1. Percentage of recovery of pm-xylene, o-xylene and toluene in Standard 1, Standard 2 and Standard 3 (concentration of 8 ppm for Standard 1, 10 ppm for Standard 2 and 12 ppm for Standard 3) by sample (a) POFN, (b) R1 and (c) R5 after recovery test using carbon disulphide as eluent.

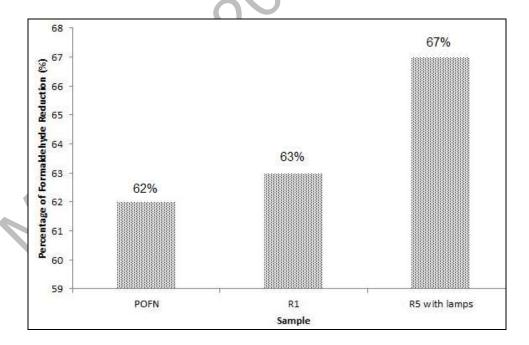


Figure 2. Percentage of formaldehyde concentration reduction by POFN (100% palm oil fiber), R1 (90% palm oil fiber: 10% titanium dioxide and R5 (50% palm oil fiber: 50% titanium dioxide). Only R5 was tested using reading lamps as source of light in the test chamber.

#### Conclusion

Palm oil fiber/titanium dioxide composite powder has successfully act like commercial activated carbon with percentage of recovery obtained more than 90% as required by the standard method used by NIOSH Malaysia. From the results obtained, a combination between adsorption and photocatalytic process is a promising solution to act as adsorbent and air pollutant reducer. The palm oil fiber/titanium dioxide composite acts as a photocatalyst that oxidized formaldehyde into carbon dioxide and also reduced the concentration of formaldehyde. The capability of the palm oil fiber composite enhance by the amount of the TiO<sub>2</sub> added therefore, the produced palm oil fiber/TiO<sub>2</sub> composite is capable to act as adsorbent and air pollutant reducer, simultaneously.

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## References

- 1. Katsoyiannis, A., Leva, P. and Kotzias, D., (2008). VOC and carbonyl emissions from carpets: A comparative study using four types of environmental chambers. *Journal of Hazardous Materials*, 152: 669–676.
- 2. Chang, C.T. and Chen, B.Y. (2008). Toxicity assessment of volatile organic compounds and polycyclic aromatic hydrocarbons in motorcycle exhaust. *Journal of Hazardous Materials*, 153: 1262–1269.
- 3. Wolkoff, P. and Nielsen, G. D. (2010). Non-cancer effects of formaldehyde and relevance for setting an indoor air guideline. *Environmental International*, 36 (7): 788–799.
- 4. Pala, M., Ugolini, D., Ceppi, M., Rizzo, F., Maiorana, L., Bolognesi, C., Schilirò, T., Gilli, G., Bigatti, P., Bono, R. and Vecchio, D. (2008). Occupational exposure to formaldehyde and biological monitoring of Research Institute workers. *Cancer Detection and Prevention*, 32 (2): 121–126.
- 5. Chen, J. and Poon, C. (2009). Photocatalytic construction and building materials: From fundamentals to applications. *Building and Environment*, 44 (9): 1899 1906.
- 6. Sanjuán-herráez, D., De Osa, S., Pastor, A. and De Guardia, M. (2014). Air monitoring of selected volatile organic compounds in wineries using passive sampling and headspace-gas chromatography mass spectrometry. *Microchemical Journal*, 114: 42–47.
- 7. Zaitan, H., Korrir, A., Chafik, T. and Bianchi, D. (2013). Evaluation of the potential of volatile organic compound (di-methyl benzene) removal using adsorption on natural minerals compared to commercial oxides. *Journal of Hazardous Materials*, 262: 365–376.
- 8. Ewlad-Ahmed, A. M., Morris, M. A., Patwardhan, S. V. and Gibson, L. T. (2012). Removal of formaldehyde from air using functionalized silica supports. *Environmental Science and Technology*, 46: 13354 13360.
- 9. Yu, Q. L. and Brouwers, H. J. H. (2009). Indoor air purification using heterogeneous photocatalytic oxidation. Part I: Experimental study. *Applied Catalysis B: Environmental*, 92(3–4): 454 461.
- 10. Zhao, J. and Yang, X. (2003). Photocatalytic oxidation for indoor air purification: A literature review. *Building and Environment*, 38 (5): 645 654.
- 11. Maira, A. J., Yeung, K. L., Lee, C. Y., Yue, P. L. and Chan, C. K. (2000). Size effects in gas-phase photo-oxidation of trichloroethylene using nanometer-sized TiO<sub>2</sub> catalysts. *Journal of Catalysis*, 192 (1): 185 196.
- 12. Tseng, J. Y., Chang, C. Y., Chang, C. F., Chen, Y. H., Chang, C. C., Ji, D. R., Chiu, C. Y. and Chiang, P. C. (2009). Kinetics and equilibrium of desorption removal of copper from magnetic polymer adsorbent. *Journal of Hazardous Materials*, 171 (1–3): 370 377.
- 13. Thammakhet, C. and Muneesawang, V. (2006). Cost effective passive sampling device for volatile organic compounds monitoring. *Atmospheric Environment* 40: 4589 4596.
- 14. Ciabini, L., Santoro, M., Gorelli, F. A., Bini, R., Schettino, V. and Raugei, S. (2007). Triggering dynamics of the high-pressure benzene amorphization. *Nature Materials*, 6: 39 43.
- 15. Quiroz Torres, J., Royer, S., Bellat, J. P., Giraudon, J. M. and Lamonier, J.-F. (2013). Formaldehyde: catalytic oxidation as a promising soft way of elimination. *ChemSusChem*, 6 (4): 578 592.
- 16. Li, F. B., Li, X. Z., Ao, C. H., Lee, S. C. and Hou, M. F. (2005). Enhanced photocatalytic degradation of VOCs using Ln<sup>3+</sup>-TiO<sub>2</sub> catalysts for indoor air purification. *Chemosphere*, 59 (6): 787 800.