

# Indonesian Journal of Chemical Science and Technology (IJCST)

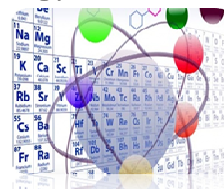
State University of Medan, <https://jurnal.unimed.ac.id/2012/index.php/aromatika>

IJCST-UNIMED 2023, Vol. 08, No. 1 Page; 15 – 21

Received : Oct 11<sup>th</sup>, 2024

Accepted : Jan 11<sup>th</sup>, 2025

Web Published : Jan 31<sup>st</sup>, 2025



## Adsorption and Desorption Properties of Beta Carotene in Crude Palm Oil on Activated Carbon Composites of Oil Palm Empty Fruit Bunches with MOFs-Cu(TAC)

Frengky Sanjaya Ginting\*, Yunita Dwi Utami, Desika Devani Br Surbakti, Dika Fahreza, Wella Apriwidayanti, Therecia Fricillia Ginting, Putri Faradilla, Rini Selly, Jasmedi, Moondra Zubir

Chemistry Department, Faculty of Mathematics and Natural Science, Universitas Negeri Medan, Medan 20221, Indonesia

\*Corresponding author : [gintingfrengky95@gmail.com](mailto:gintingfrengky95@gmail.com)

### ABSTRACT

*Oil palm bunches Empty fruit bunches are the main lignocellulosic solid waste that has not been optimally utilized, so many empty bunches are not processed. Unprocessed EFB causes a foul odor and becomes a place for flies to nest. Thus, it is considered as waste that pollutes the environment. Adsorption is a popular new method to reduce heavy metal content and waste in water, in addition the adsorption method is also effective and efficient in terms of the absorption process, and can also be a regeneration adsorbent. This study began with the preparation of empty oil palm bunches which were then carbonized and activated with  $H_3PO_4$ , then synthesized with MOFs-Cu(TAC). The final stage was tested for absorption by optimizing mass and time. The XRD pattern shows sharp peaks that appear on the graph indicating metal contact and the KA-Cu(TAC) composite has a good and regular crystal structure. The KA-Cu(TAC) composite has great potential as an alternative adsorbent to improve the quality of palm oil because it has good absorption.*

Keywords: Activated carbon, MOFs, Composite, Adsorption, Beta-carotene

### 1. INTRODUCTION

Based on statistical data from the Central Statistics Agency and the Directorate General of Horticulture (2017), North Sumatra is the third largest palm oil cultivator in Indonesia with a production level of 12.02% of the total 1,758,936 tons. As palm oil production increases, the amount of waste produced also increases. The operation of palm oil mills produces main products in the form of CPO (Crude Palm Oil), PKO (Palm Kernel Oil) and PK (Palm Kernel), as well as by-products in the form of solid waste, liquid waste and air pollutants.<sup>1</sup> According to Sopiah et al 2017, empty oil palm bunches are the main lignocellulosic solid waste which has not been utilized optimally so that many empty bunches are not

processed. Unprocessed EFB produces an unpleasant odor and becomes a place for flies to nest. Therefore, it is considered waste that can pollute the environment and spread pathogens.<sup>2</sup>

Based on research by Jasmidi et al 2022, adsorption is a popular new method for reducing the content of heavy metals and waste in water because of its simple nature and low cost of use, besides that the adsorption method is also effective and efficient in terms of absorption. process, and can also be a regeneration adsorbent.<sup>3</sup> Phosphoric acid ( $H_3PO_4$ ) was chosen as the activator because it does not pollute the environment and the process of neutralizing activated carbon products is easy, namely just washing with water.<sup>4</sup> The most widely used adsorbent is activated carbon. Activated carbon is carbon that is processed through heating carbon-containing materials at high temperatures but is not oxidized, so it has high absorption or adsorption capacity. Activated carbon is widely used as an adsorbent and generally has the capacity to adsorb organic molecules.<sup>5</sup> Crude Palm Oil (CPO) consists of the main ingredient, namely triglycerides (94%), and other additional ingredients are tocopherols, sterols, phosphatides, and carotenoids. CPO contains carotenoid compounds of 500-700 ppm (0.5-0.7 kg per ton).<sup>6</sup> According to Rahardja 2022, CPO is the result of palm oil factory processing which comes from palm fresh fruit bunches (FFB). CPO has a boiling point of around  $240^{\circ}C$  compared to water which can boil at  $100^{\circ}C$ .<sup>7</sup>

One innovative way to improve adsorption results is to synthesize composite materials with the aim of achieving new adsorption characteristics such as high pore volume and porosity. Metal organic frameworks (MOFs)-based carbon composites have attracted attention due to their high surface area and reactivity as well as their extraordinary adsorption capacity and thermal stability.<sup>8</sup> In this research, activated carbon from empty oil palm fruit bunches with a metal organic frame was used from Cu metal and the organic ligand terephthalic acid (TAC). The choice of Cu as the central metal in the Ministry of Finance is due to its selectivity and high adsorption capacity.<sup>9</sup> Cu metal in the environment can come from metal welding, industrial and domestic waste, mining, and mineral washing.<sup>10</sup> According to Natalia 2020, Terephthalic acid,  $C_8H_6O_4$ , also known as 1,4 benzendicarboxyl acid, p-phthalic acid and p-benzendicarboxyl acid consists of a benzene ring with a carboxyl group on carbons 1 and 4.<sup>11</sup> MOFs have a strong and highly porous structure that can accommodate various guest molecules.<sup>12</sup> In this study, the composite of activated carbon from oil palm empty fruit bunches with MOFs-Cu(TAC) was studied to understand the effect of activated carbon and terephthalic acid (TAC) composition on the adsorption and desorption properties of beta carotene in CPO.

## **2. EXPERIMENTAL**

### *2.1. Chemicals, Equipment and Instrumentation*

#### *2.1.1 Research equipment*

The equipment used in this study included glassware, reflux, grinder, 200 mesh sieve, vacuum pump, analytical balance, oven, furnace, desiccator, hot plate, burette, stand and clamp, XRD and UV-Vis.

#### *2.1.2 Research Materials*

The materials used in this study were empty oil palm bunches (TKKS), Zn(II) metal,  $H_3PO_4$ , TAC(terephthalic acid), HF(hydrofluoric acid),  $HNO_3$ (nitric acid),  $Cu(NO_3)_2$ (copper (II) nitrate), distilled water, filter paper, universal pH, CPO (Crude Palm Oil), 90% alcohol, KOH (Potassium hydroxide), glacial acetic acid, chloroform, KI,  $Na_2S_2O_3$ , and 1% starch solution.

## *2.2. Research Procedure*

### *2.2.1. Preparation of Empty Oil Palm Bunches*

Empty Oil Palm Fruit Bunches (EFB) are collected and taken from PT Multi Agriindo Sumatera. The collected EFB are washed using running water and dried in the sun until dry. The dried EFB are chopped into small pieces then ground using a blender and sieved with a 200 mesh sieve to produce biosorbent.<sup>13</sup>

### *2.2.2. Moisture Content of Empty Oil Palm Bunches*

Water content testing can be determined by drying the biosorbent in an oven. The petri dish that has been dried in an oven for 15 minutes at a temperature of 105°C is weighed. 2 grams of biosorbent is placed in a petri dish of known weight, then dried in an oven at a temperature of 105°C for 2 hours. After drying, the biosorbent is cooled in a desiccator for 15 minutes and reweighed until a constant weight is obtained.

### *2.2.3. Carbonization*

The dried empty oil palm bunches biosorbent is heated in a furnace at a temperature of 500° C for approximately 2 minutes. After carbonization, the biosorbent is allowed to cool naturally and transferred into a closed container.

### *2.2.4. Activation*

The carbonized carbon was prepared and weighed. A total of 10 grams of activated carbon was soaked in 100 mL of 10% H<sub>3</sub>PO<sub>4</sub> for 24 hours. The activated carbon was filtered using filter paper and a vacuum filter and then washed with distilled water until the pH was neutral. The activated activated carbon was dried for 24 hours at 105°C in an oven and then cooled and put into a closed container.<sup>14</sup>

### *2.2.5 Synthesis of Activated Carbon Composite / MOFs-Cu(TAC)*

Activated carbon, terephthalic acid and ethanol PA with a ratio of 1.8:0.6:10 were mixed, then soaked for 24 hours. The mixture was mixed with a porous polymer solution Cu-(TAC)<sub>2</sub> and refluxed at a temperature of 90 for 8 hours. Then cooled and filtered, the solid obtained was washed with distilled water until the pH was neutral.<sup>15</sup>

### *2.2.6 Determination of the Effect of Optimum Adsorption Mass on CPO*

CPO was put into five beaker glasses, each 100 mL, then 2, 4, 6, 8 and 10 grams of Cu-modified activated carbon were put into each beaker. Then the mixture was heated using a hot plate at a temperature of 60 °C and homogenized using a magnetic stirrer at a constant speed of 120 rpm for 120 minutes. Then the mixture was filtered with Whatman No. 1 filter paper. The filtrate was stored for analysis of β-carotene levels.

### *2.2.7 Determination of the Effect of Optimum Contact Time on Adsorption on CPO*

Modified activated carbon Cu and CPO with the optimum mass ratio obtained was inserted into the beaker glass. Then the mixture was heated using a hot plate at a temperature of 60°C and homogenized using a magnetic stirrer at a constant speed of 120 rpm for 30, 60, 90, 120 and 150 minutes. Then the mixture was filtered with Whatman No. 1 filter paper. The filtered activated carbon was stored for use in the desorption process, and the adsorption filtrate was stored for analysis of β-carotene levels.

### 2.2.8 Analysis of $\beta$ -carotene content determination

The CPO sample was melted first in a water bath and then given a code for each sample, then the sample was weighed as much as 0.1001gr and put into a 25 ml measuring flask, isooctane was added to the boundary mark on the flask, then homogenized until the CPO was completely dissolved, then the absorbance of the sample was measured using a UV-Vis spectrophotometer at a wavelength of 446 nm. After obtaining the beta carotene absorbance value, the beta carotene content in the CPO sample can be determined using the following formula:

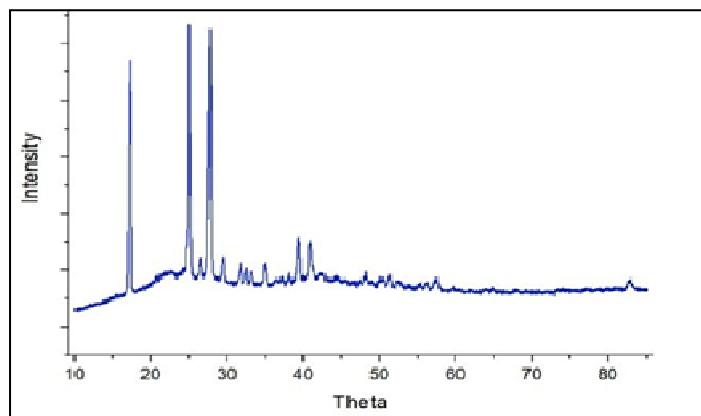
$$\text{Konsentrasi } \beta - \text{karoten (ppm)} = \frac{A \times 383 \times 25}{w \times 100}$$

With , A : Absorbance and w : Sample weight

## 3. RESULTS AND DISCUSSION

### 3.1. Analysis of Characterization Results

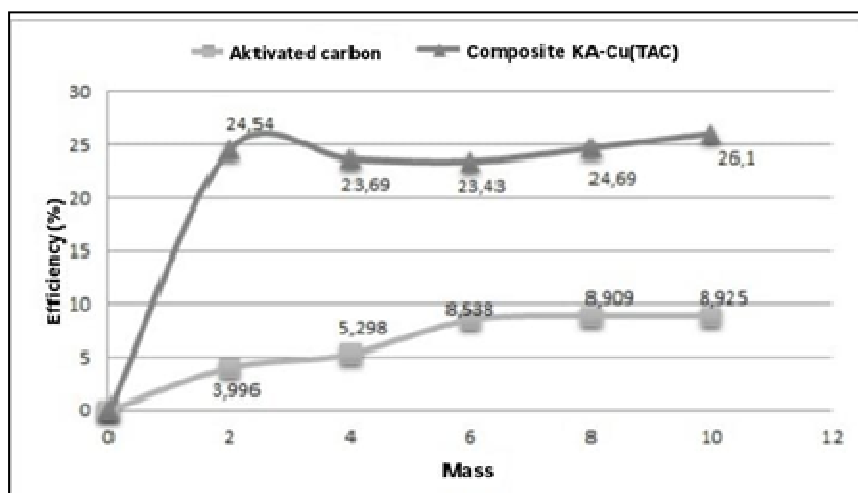
The result of carbonization is a carbon material with a microporous structure that gives carbon the ability to adsorb various types of molecules based on their particle size, making it an ideal material for adsorption applications. The sharp peaks appearing on the graph indicate the presence of metal contact and the KA-Cu(TAC)<sub>2</sub> composite has a good and regular crystal structure. The large number of peaks indicates the presence of various crystal planes in the sample, which shows the complexity of the crystal structure of this composite.



**Figure 1.** Composite XRD Pattern KA- Cu(TAC)<sub>2</sub>

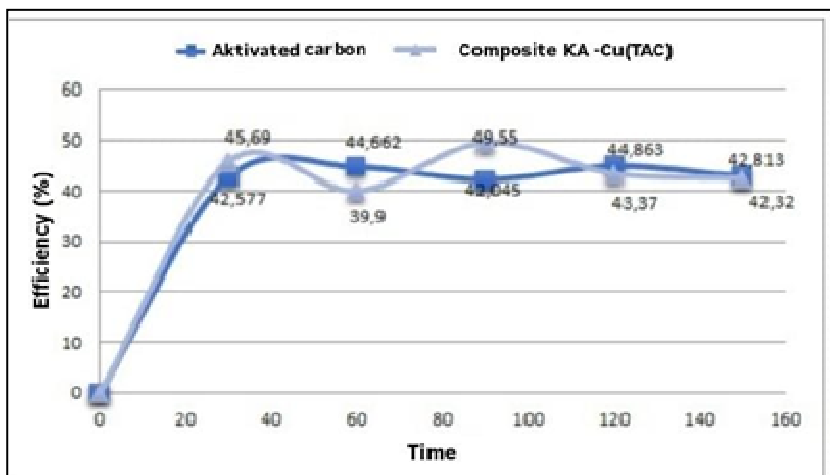
These sharp peaks are seen appearing at 2 theta in the range of 15°-40°. The triclinic crystal system is characterized by three main crystal axes that are not in the same direction and have different lengths. While the monoclinic crystal system has one rotation or mirror axis. The monoclinic crystal system is more regular than the triclinic because it only has one axis of symmetry. This shows that the use of activated carbon in the synthesis of KA-MOFs Cu(TAC) has an effect on the formation of a more regular crystal structure.

Based on the experimental results shown in the graph, the efficiency of activated carbon absorption increases with increasing mass used so that the optimum condition of  $\beta$ -carotene has not been found. And in the KA-Cu (TAC) Composite there was a decrease in the mass of 4 grams and 6 grams, but there was an increase in the mass of 8 grams and 10 grams.



**Figure 2.** Adsorbent mass dependence of beta carotene adsorption efficiency

The KA-Cu (TAC) Composite has better performance in absorbing beta-carotene from crude palm oil (CPO) compared to activated carbon. This is indicated by the higher beta-carotene absorption efficiency in the KA-Cu (TAC) Composite, especially at a larger adsorbent mass. This increase in absorption efficiency is due to the larger specific surface area and more regular pore structure in the KA-Cu (TAC) Composite, allowing stronger interactions between the adsorbent and beta-carotene molecules. Thus, the KA-Cu (TAC) Composite has great potential as an alternative adsorbent to improve the quality of palm oil.



**Figure 3.** Time dependence of beta-carotene absorption efficiency

It can be seen in the graph above that activated carbon reaches the optimum efficiency point at 44.662% while the KA-Cu(TAC) Composite is optimum at an efficiency of 49.55 with a time of 90 minutes. Based on the results of existing research, the KA-Cu(TAC) composite shows superior potential compared to activated carbon in the beta-carotene adsorption process on CPO. Modification of activated carbon by adding

Cu ions and TAC matrix not only increases the surface area and pore volume, but also creates new active sites that are more specific for binding beta-carotene molecules. This allows the KA-Cu(TAC) composite to achieve higher adsorption efficiency, better selectivity, and better stability compared to conventional activated carbon. In addition, the use of empty oil palm bunch waste as a composite raw material also provides added value in terms of sustainability and economy

#### 4. CONCLUSION

In the manufacture of KA-MOFs Cu(TAC) composites, activated carbon serves to provide space for metals and ligands to bond with each other, resulting in many open pores. Terephthalic acid, plays an important role as a ligand, can bind two metal atoms, so that the interaction between ligands, carbon, and metals will increase the surface area, pore size, and cell volume. So that the number of open pores will also increase. The results of XRD characterization show that KA-MOFs Cu(TAC) forms a crystal structure characterized by the appearance of sharp peaks at 2 theta values. KA-Cu(TAC)<sub>2</sub> composites have great potential as alternative adsorbents to improve the quality of palm oil as seen from the increase in the efficiency of beta carotene absorption that has been tested.

#### ACKNOWLEDGEMENT

We would like to express our deepest gratitude to our supervisors who have provided invaluable guidance and direction for us during the research process. We would also like to thank LPPM UNIMED for supporting our research by providing funding. Your support means a lot to us.

#### REFERENCES

- 1 Ilmannafian, A. G., Lestari, E., & Khairunisa, F. (2020). Pengolahan Limbah Cair Pabrik Kelapa Sawit Dengan Metode Filtrasi Dan Fitoremediasi Menggunakan Tanaman Eceng Gondok (*Eichhornia Crassipes*). *Jurnal Teknologi Lingkungan*, 21(2), 244-253.
- 2 Sopiah, N., Prasetyo, D., & Aviantara, D. B. (2017). Pengaruh aktivasi karbon aktif dari tandan kosong kelapa sawit terhadap adsorpsi kadmium terlarut. *Jurnal Riset Teknologi Pencegahan Pencemaran Industri*, 8(2), 55-66.
- 3 Jasmidi, J., Selly, R., Ningsih, A. P., Nasution, H. I., Rahmah, S., & Zubir, M. (2022, November). Efficiency of ammonia adsorption by metal modified activated carbon of oil palm empty bunches. In *AIP Conference Proceedings* (Vol. 2659, No. 1). AIP Publishing..
- 4 Husin, A., & Hasibuan, A. (2020). Studi pengaruh variasi konsentrasi asam posfat (H<sub>3</sub>PO<sub>4</sub>) dan waktu perendaman karbon terhadap karakteristik karbon aktif dari kulit durian. *Jurnal Teknik Kimia USU*, 9(2), 80-86..
- 5 Syauqiah, I., Amalia, M., & Kartini, H. A. (2011). Analisis variasi waktu dan kecepatan pengaduk pada proses adsorpsi limbah logam berat dengan arang aktif. *Info-Teknik*, 12(1), 11-20.
- 6 Lestari, W.W., Yunita, L., Saraswati, T.E., Heraldy ,E.,Khafidhin ,M.A., Arrozi ,U.S.F., Kadja ,G.T.M.(2021). Fabrication of composite materials MIL-100(Fe)/Indonesian activated natural zeolite as enhanced CO<sub>2</sub> capture material,” *Chem. Pap.*, 75(7), 3253–3263.
- 7 Rahardja, I. B., Gumilang, R. N. R., Rantawi, A. B., & Saputra, H. (2022, October). Komparasi karakteristik laju panas, dingin & massa jenis pada crude palm oil (CPO), minyak goreng serta air. In *Prosiding Seminar Nasional Penelitian LPPM UMJ* (Vol. 1, No. 1).
- 8 Harahap, I.S., Wahyuningsih, P and Amri, Y. (2020). Analisa Kandungan Beta Karoten Pada Cpo (Crude Palm Oil) Di Pusat Penelitian Kelapa Sawit (Ppks) Medan Menggunakan Spektrofotometri Uv-Vis,” *Quim. J. Kim. Sains dan Terap.* 2 (1), 9–13,.
- 9 Zhang, Y., Chen, Z., Liu, X., Dong, Z., Zhang, P., Wang, J., ... & Deng, S. (2019). Efficient SO<sub>2</sub> removal using a microporous metal-organic framework with molecular sieving effect. *Industrial & Engineering Chemistry Research*, 59(2), 874-882.

- 10 Indah, D. R. (2020). Adsorpsi Logam Tembaga (Cu) Pada Karbon Baggase Teraktivasi Natrium Hidroksida (NaOH). *Jurnal Ilmiah IKIP Mataram*, 7(1), 20-28.
- 11 Natalia, M., & Hazrifawati, W. (2020). PRARANCANGAN PABRIK ASAM TEREPTALAT DENGAN PROSES OKSIDASI PARAXYLENE KAPASITAS 300.000 TON/TAHUN. *JURNAL TUGAS AKHIR TEKNIK KIMIA*, 3(2), 43-48.
- 12 Solis, K. L. B., Kwon, Y. H., Kim, M. H., An, H. R., Jeon, C., & Hong, Y. (2020). Metal organic framework UiO-66 and activated carbon composite sorbent for the concurrent adsorption of cationic and anionic metals. *Chemosphere*, 238, 124656.
- 13 Allwar, A. (2018). Preparation and characteristics of highly microporous activated carbon derived from empty fruit bunch of palm oil using KOH activation. *Rasayan Journal of Chemistry*, 11(1), 280-286.
- 14 Zubir, M., Muchtar, Z., Syahputra, R. A., Sudarma, T. F., Nasution, H. I., Lubis, R. A. F., ... & Sandi, K. (2021, **March**). Characterization of Modified Fe-Cu Nanoparticle Activated Carbon Derived of Oil Palm Empty Bunches. In *Journal of Physics: Conference Series* (Vol. 1819, No. 1, p. 012020). IOP Publishing.
- 15 Muñoz-Senmache, J. C., Kim, S., Arrieta-Pérez, R. R., Park, C. M., Yoon, Y., & Hernández-Maldonado, A. J. (2020). Activated carbon–metal organic framework composite for the adsorption of contaminants of emerging concern from water. *ACS Applied Nano Materials*, 3(3), 2928-2940..