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Synthesis of Cu-(TAC) Composite with Oil Palm Empty Fruit Bunch Waste Activated Carbon Through the Adsorption Mechanism of β-Carotene

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ABSTRACT

This study aims to determine the adsorption and desorption abilities of activated carbon and Cu-(TAC) composites in the β-carotene adsorption process on Crude Palm Oil (CPO). Oil Palm Empty Fruit Bunches (EFB) are used as activated carbon and modified with MOFs Cu-(TAC). Activated carbon and Cu-(TAC) composites were characterized by XRD, SEM-EDX, and BET. The concentration of β-carotene absorbed during the adsorption process was analyzed using a UV-Vis spectrophotometer. The variations used to determine the optimum conditions for absorption of β-carotene were the mass variation of the adsorbent and the variation in the contact time between the adsorbent and adsorbate. The results of the characterization of activated carbon showed a sharp absorption in the presence of O-H, C-H and C-O groups indicating the presence of cellulose. Activated carbon is amorphous and the Cu-(TAC) composite has a crystal structure and its pore size is mesoporous. The optimum conditions for the use of activated carbon for β-carotene adsorption were the mass variation of 8 grams with 0.495 ppm of β-carotene and contact time at 120 minutes with 2.605 ppm of β-carotene. The optimum condition of the Cu-(TAC) composite in the β-carotene adsorption process was at 4 gram mass variation with 1.026 ppm β-carotene content and optimum contact time at 60 minutes with 6.384 ppm β-carotene content. The ability of desorption can be seen from the percentage of desorption showing activated carbon in the 150th minute with 96.252% while in the Cu-(TAC) composite in the 30th minute with 88.188%.

Keywords : Adsorption, β-carotene, Cu-(TAC) Composite, Activated carbon

1. INTRODUCTION

Crude palm oil (CPO) is Indonesia's main agricultural product, both as a raw material for cooking oil and as an export product. In the processing of CPO, the constraints that are often encountered are mainly related to the content of free fatty acids and beta carotene. 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) [3,13].

Activated carbon has a large adsorption capacity and can be regenerated. The large adsorption capacity is due to the large surface area, high porosity, and functional groups such as carboxyl, carbonyl, hydroxyl on the activated carbon surface [12]. Activated carbon is usually used for the adsorption of organic compounds because of its large porosity, hydrophobicity and relatively low cost [7].

Combining MOFs with activated carbon into a composite material which shows the positive characteristics of both materials. Growth of MOFs in activated carbon to increase the stability of MOFs [1,9]. MOFs consist of combining metal ions with organic ligands which are crystalline materials and have a flexibility that comes from a framework built with coordination bonds. MOFs have a high surface area and large frame volume [14].

2. EXPERIMENTAL

2.1. Chemicals, Equipment and Instrumentation

The equipment used in this study included glassware, analytical balance, thermometer, grinder, 200 mesh sieve, oven, furnace, hotplate, desiccator, X-ray diffractometer (XRD) and UV-Vis spectrophotometer. The materials used in this study included: empty palm oil bunches (EFB) from PTPN II Medan, CPO (Crude Palm Oil), CuSO4, FeSO4, distilled water, KOH, KI, isooctane, isopropanol, neutral alcohol, phenolphthalein indicator, paper filter Whatman No.1, Cu Metal, Terrephthalic Acid (TAC), and ethanol.

2.2. Research Procedure

2.2.1 OPEFB Activated Carbon Synthesis

In this study, activated carbon was made from OPEFB in a furnace at 500°C for 2 minutes, then activated carbon was activated with H_3PO_4.

2.2.2 Synthesis of MOFs Cu-(TAC)

Then the synthesis of MOFs Cu-(TAC) was carried out by refluxing a mixture of copper (II) nitrate solution, hydrofluoric acid, nitric acid, terephthalic acid, and distilled water with a ratio of 3:2:1:5,9:200 at 105^0C for 8 hours.

2.2.3 Modified Activated Carbon with MOFs Cu-(TAC)

Modification of activated carbon MOFs Cu(TAC) was carried out by immersing a mixture of terephthalic acid, ethanol and activated carbon with a ratio of 1:10:0.6 for 24 hours. Then the mixture was mixed with MOFs Cu(TAC) solution and refluxed at 105°C for 8 hours. Product activated carbon, MOFs Cu(TAC), and MOFs Cu(TAC) activated carbon composites were characterized by X-ray diffractometer (XRD)

2.2.4 β-carotene adsorption

Preheat the CPO sample to be used in the water bath and enter the code. 0.1 g of the sample was weighed, put into a 25 mL volumetric flask, added isooctane up to the mark of the flask mark, homogenized until the CPO was completely dissolved, then the absorbance of the sample was measured with UV. Measured with a visible spectrophotometer. After the absorbance value of beta-carotene is determined, then the beta-carotene content in the CPO sample. For variations in mass used are 4g, 6g, 8g, 10g, and 12g and for variations in contact time used 30 minutes, 60 minutes, 90 minutes, 120 minutes and 150 minutes

2.2.5 β-carotene Desorption

The determination of the desorption yield on the most optimum adsorption yield on CPO was carried out using 350 mL isopropanol and the adsorbent used was an adsorbent that had received adsorption treatment at the stage of determining the effect of the optimum contact time on previous adsorption. Isopropanol was mixed into each adsorbent and heated using a hotplate at 500 C using a magnetic stirrer at a constant speed of 180 rpm for 45 minutes. The mixture was then filtered using Whatman filter paper no.1.

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction (XRD) Characterization

Analysis using XRD (X-Ray Diffraction) aims to identify the structure and degree of crystallinity of Activated Carbon, Cu-(TAC) MOFs, and Cu-(TAC) Composites. Following are the XRD results of Activated Carbon, Cu-(TAC) MOFs, and Cu-(TAC) Composites:

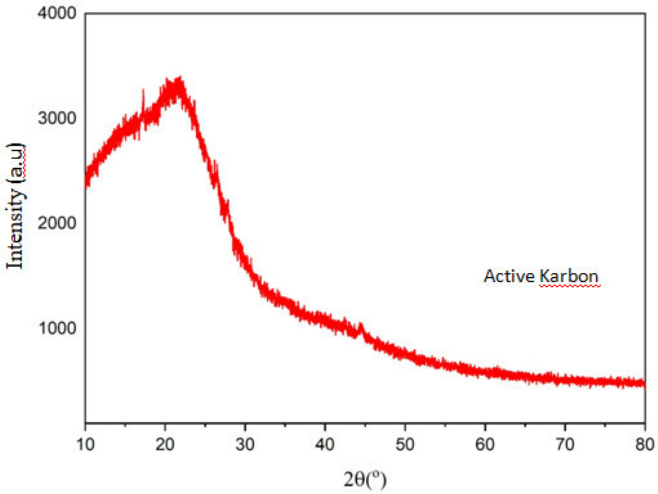


Figure 1. XRD pattern of Activated Carbon

The active carbon XRD pattern shows an amorphous material structure where the amorphous structure is a more reactive structure and is suitable for application as a biosorbent. Amorphous also has high purity, small particle size, and large surface area [5]. Meanwhile, Cu-(TAC) MOFs and Cu-(TAC) Composites have a crystalline material structure. On activated carbon, a sharp peak appears at 2 theta around 30º-40º. MOFs Cu-(TAC) and Cu-(TAC) composites show a diffraction peak at 2 theta with the appearance of 4 sharp peaks in the 2 theta region around 15º-30º which is a Miller index which has a Triclinic and Monoclinic crystal system.

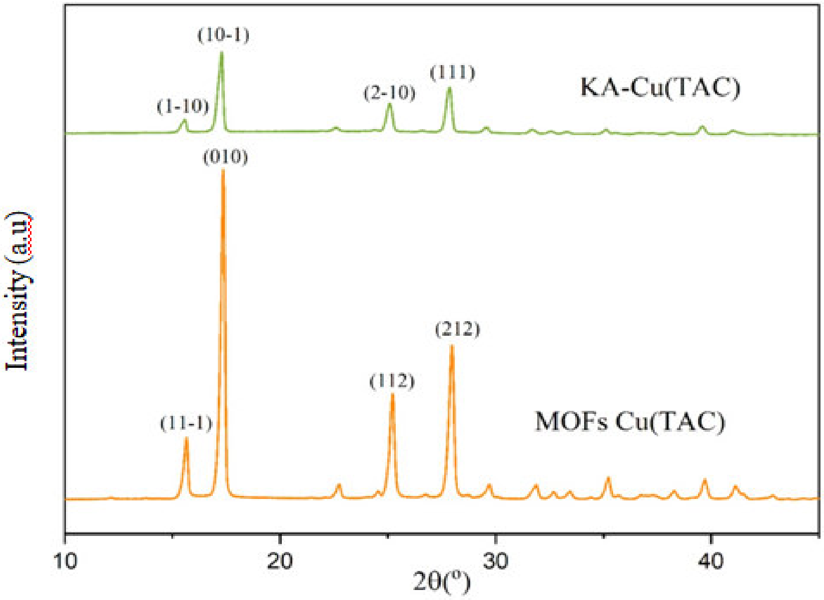
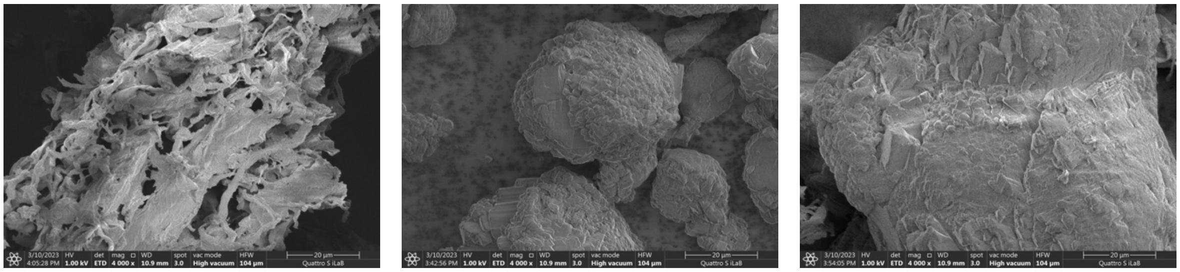


Figure 2. XRD pattern of MOFs Cu-(TAC) and Cu-(TAC) Composite

3.2 Scanning Electron Microscopy (SEM) Characterization

Morphological analysis of Activated Carbon, MOFs Cu-(TAC) and Composite Cu-(TAC) using SEM (Scanning Electron Microscopy) with 4000x magnification to determine the surface shape of Activated Carbon, MOFs Cu-(TAC) and Composite Cu-(TAC).



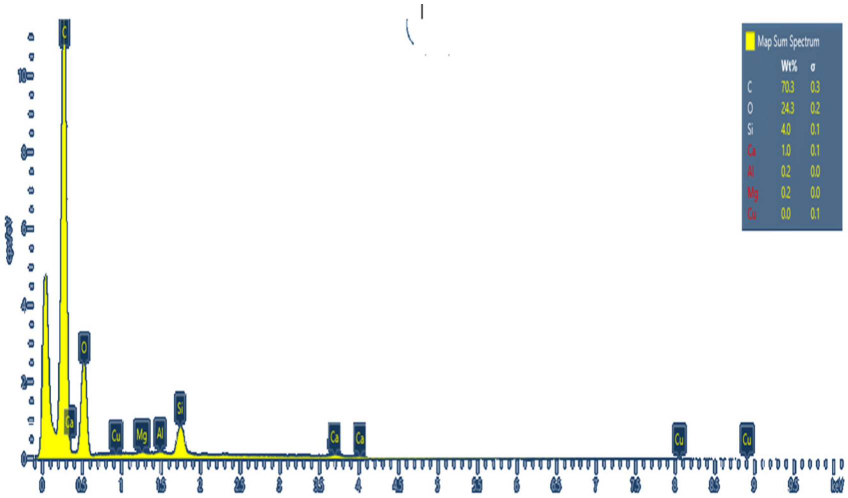
(a) (b) (c)

Figure 3. SEM analysis (a) Activated Carbon, (b) MOFs Cu-(TAC), (c) Composite Cu-(TAC)

Based on Figure 3, SEM morphology of activated carbon has a similar shape, smaller size. Cu-(TAC) composites have more pores and are more open. The more pores, the greater the ability of activated carbon for the adsorption process. In Figure 3.3 (b) the SEM morphology of MOFs has several forms because this sample has 2 crystal systems, the size of which is smaller than the two samples. In Figure 3 (c) the SEM morphology of the Cu-(TAC) composite has the larger size of the two samples, the modified activated carbon looks more homogeneous than the MOFs. This happened because the ethanol solvent used in the Cu-(TAC) composite had an influence on the resulting crystal morphology. The less amount of ethanol used, the rougher and more irregular the crystal morphology.[12] In addition to increasing the surface area of activated carbon, this modification makes the carbon structure more regular and the spacing between carbons more homogeneous.

3.3 *Energy Dispersi X-Ray (EDX) Characterization*

Characterization using EDX (Energy Dispersion X-Ray) in this study is used to identify the elements contained in Activated Carbon, MOFs Cu-(TAC), Composite Cu-(TAC) with the basic principle that each element has a unique atomic structure which allows for a unique series of peaks in its electromagnetic emission spectrum. The EDX characterization shows the weight percent (Wt %) and atoms (At %) of each element that makes up the sample.



Map Sum Spectrum

	Wt%	σ
C	70.3	0.3
O	24.3	0.2
Si	4.0	0.1
Ca	1.0	0.1
Al	0.2	0.0
Mg	0.2	0.0
Cu	0.0	0.1

Figure 4. Characterization of EDX of Activated Carbon OPEFB

Table 2. EDX Data Elemental content in Activated Carbon OPEFB

	C	**O**	**Si**	**Ca**	**Al**	**Mg**
Wt %	70.3	24.3	4.0	1.0	0.2	0.0
At %	0.3	0.2	0.1	0.1	0.0	0.0

Table 2 shows that the carbon content (C) is the highest element content contained in active carbon with a weight (Wt%) of 70.3% and an atomic percent (At%) of 0.3%. The presence of other mineral content such as silicon (Si), calcium (Ca), aluminum (Al), and magnesium (Mg) contained in this activated carbon as impurities caused by the carbonization process. The presence of mineral content in activated carbon can clog pores thereby affecting its adsorption power.

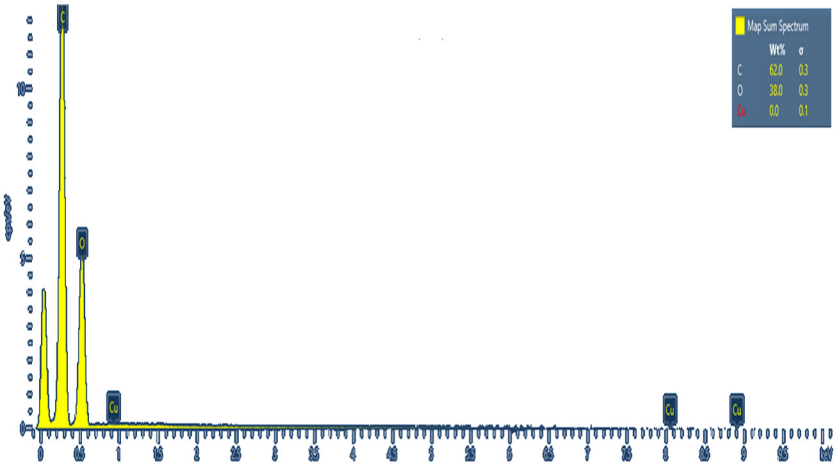


Figure 5. Characterization of MOFs Cu-(TAC) EDX

Table 3. EDX Data Elemental content in MOFs Cu-(TAC)

	C	**O**	**Cu**
Wt %	62.0	38.0	0.0
At %	0.3	0.3	0.1

Table 3 shows the highest elemental content of carbon (C) in MOFs with a weight (Wt%) of 62.0% and an atomic percent (At%) of 0.3%. In addition, there is also a Cu content but with a low central atom (At%), namely 0.1%. This shows the success of the copper elements mixed perfectly when refluxed.

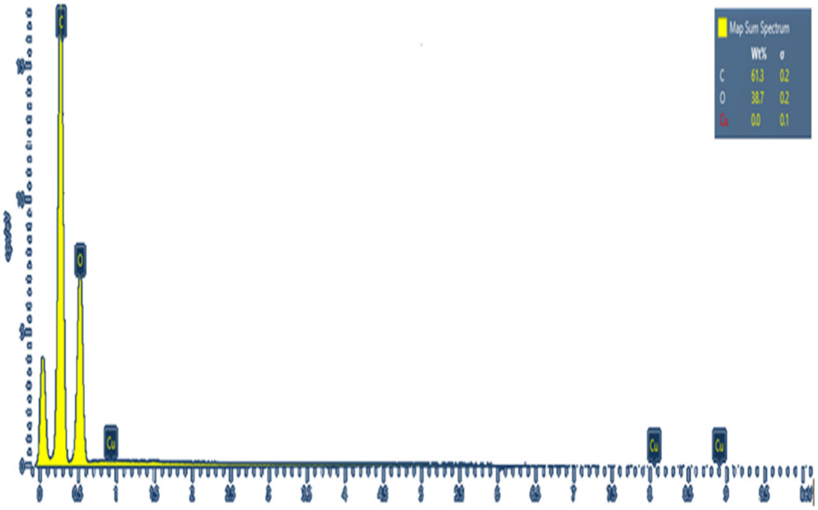


Figure 6. EDX Characterization of Composites Cu-(TAC)

Table 4. EDX Data Elemental content in Composites Cu-(TAC)

	C	**O**	**Cu**
Wt %	61.8	38.7	0.0
At %	0.3	0.3	0.1

Table 4. shows the highest elemental content of carbon (C) in the Cu-(TAC) Composite with a weight (Wt %) of 61.8% and a central atom (At %) of 0.3%. The carbon content in Cu-(TAC) Composite is reduced compared to activated carbon and MOFs Cu-(TAC) and other minerals contained in activated carbon are also lost due to activation and modification. The presence of Cu content but with a low percentage indicates the success of the copper element to mix perfectly when refluxed in the modification process.

3.4 Pore Characterization

Pore characterization using the BET Instrument aims to determine the surface area, volume, pore size, pore type, and identification of activated carbon adsorption isotherms, MOFs Cu-(TAC) and Cu-(TAC) composites. The porous structure of activated carbon, MOFs Cu-(TAC) and Cu-(TAC) composites can be determined using adsorption-desorption measurements of nitrogen gas (N_2). These measurements can show isotherm curves of activated carbon, MOFs Cu-(TAC) and Cu-(TAC) composites.

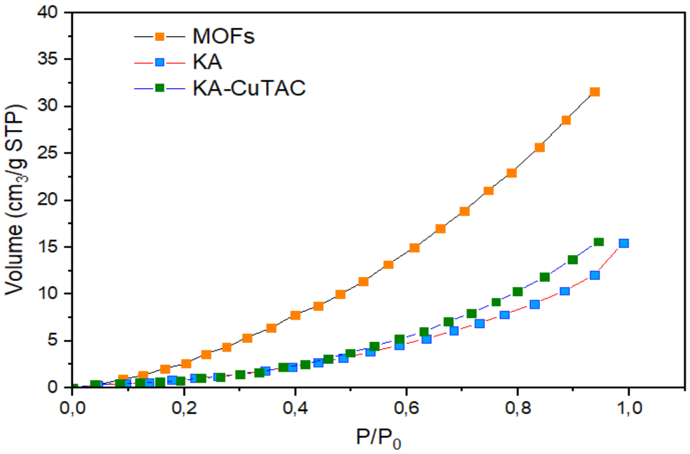


Figure 7. Isotherm Adsorption of Activated Carbon, Cu-(TAC) MOFs, and Cu-(TAC) Composites

Based on the classification of adsorption isotherms, MOFs isotherm curves, activated carbon and Cu-(TAC) composites show type III isotherms and have mesoporous sizes [2]. The surface area of the Cu-(TAC) Composite also increased from 14.891 m^2g^{-1} to 19.06 m^2g^{-1}. The increase in the surface area of Cu-(TAC) Composite carbon occurs due to the reaction of activated carbon with MOFs during the modification process which not only expands the pore surface but also activates the pore edges. The inclusion of MOFs with a predetermined amount on activated carbon affects the pore volume so that it can be interpreted that MOFs occupy the pore surface and enter into the pore thereby expanding the pore surface of the Cu-(TAC) Composite.

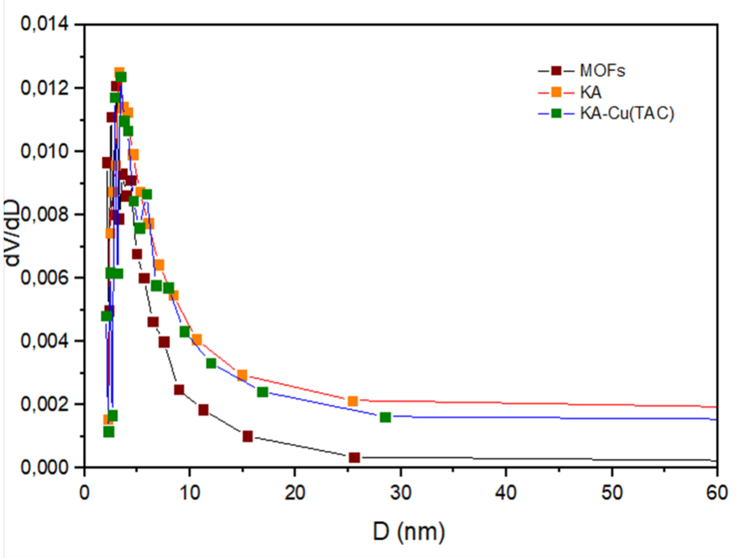


Figure 8. Pore Distribution of Activated Carbon, Cu-(TAC) MOFs, and Cu-(TAC) Composites

Figure3.8 shows that the pore size in activated carbon, MOFs Cu-(TAC), and Composite Cu-(TAC) is not homogeneous, as can be seen from the large variation in pore size between 2 – 50 nm on the graph.

Table 5. Pore Properties of MOFs, Activated Carbon and Cu-(TAC) Composites

Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
KA	14.89	0.039	10.47
MOFs Cu-(TAC)	48.40	0.068	5.61
Composite Cu-(TAC)	19.06	0.037	7.69

In table 5 it can be seen that the pore size of Activated Carbon, Cu-(TAC) MOFs, and Cu-(TAC) Composites are not homogeneous. The widest pore size is owned by activated carbon with 10.47 nm and the smallest pore size is owned by MOFs Cu-(TAC) with an area of 5.61 nm. However, the highest surface area is owned by MOFs Cu-(TAC) with a surface area of 48.40 m^2/g.

3.5β-carotene adsorption

3.5.1 β-Carotene Adsorption Optimum Mass

Determination of the optimal carbon mass was carried out to investigate how much sample mass was used to absorb β-carotene into CPO using several mass variations. Mass variations were used to determine optimal conditions for β-carotene absorption. In this study the variations in the mass used were 4 g, 6 g, 8 g, 10 g, and 12 g for both activated carbon and Cu-(TAC) composites. Adsorption was carried out at the same temperature, stirring speed and box time for the mass of each sample. The levels of β-carotene absorbed in each sample can be seen in the following figure.

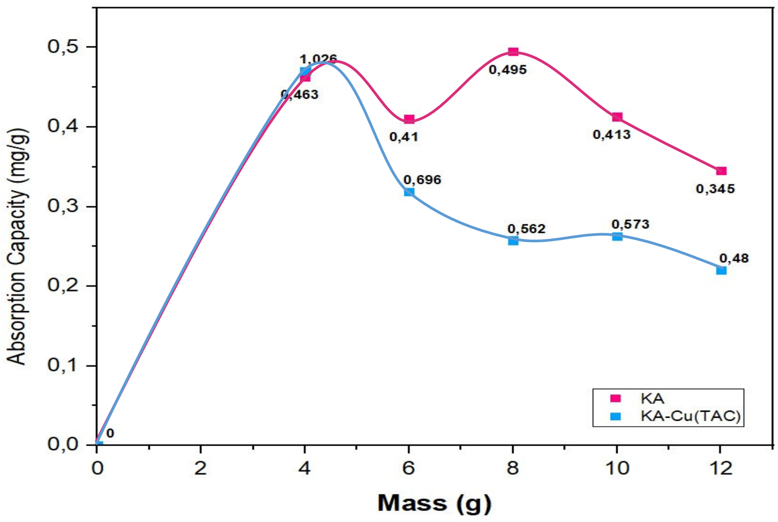


Figure 9. Mass Variation of β-Carotene Adsorption Absorption Capacity

Based on Figure 3.9, it can be seen that the optimum mass of activated carbon to adsorb β-carotene is 8g and 4g for adsorbing Cu-(TAC) composites. The optimal amount of activated carbon adsorbed on activated carbon was 0.495 less than the amount of β-carotene adsorbed on the Cu-(TAC) composite, which was 1.026 ppm. When compared with all the mass variations of activated carbon with Cu-(TAC) composite, it can be seen that the Cu-(TAC) composite absorbs more β-carotene than activated carbon. Composite activated carbon is a more effective adsorbent than activated carbon because activated carbon has a higher adsorption capacity because it is made from a mixture of materials containing carbon and cellulose. This mixture is in the form of a porous solid and has a large surface area, so it functions to absorb harmful toxic substances [6].

If a solution contains more than one type of adsorbent, then these substances will compete to occupy the surface or pores of the adsorbent. The bleaching process combined with heat treatment and activated carbon can produce new coloring compounds such as tocopherol oxidation products. Activated carbon is not classified as a selective adsorbent, so other dyes will also be adsorbed, causing the activated carbon to absorb more or less β-carotene. Decreasing levels of β-carotene after the optimum mass is reached, is possible because the adsorbent has reached its absorption saturation capacity. thereby reducing the adsorption capacity of the adsorbent [10].

3.2.2 Optimum Contact Time of β-Carotene Adsorption

Contact time can also affect performance and absorption [11]. So that it will affect the effectiveness of a sample. Adsorption of β-carotene on CPO using several time variations to determine the optimal contact time in the absorption of β-carotene after obtaining the optimal mass. Variations of time used were 30 minutes, 60 minutes, 90 minutes, 120 minutes and 150 minutes both in activated carbon and Cu-(TAC) composites. Adsorption was carried out with the same temperature, treatment and stirring for each contact time and sample. In Figure 10 it can be seen that the highest adsorbed β-carotene value on activated carbon was found in the 120th minute and 60th minute in the Cu-(TAC) composite. The amount of β-carotene adsorbed on activated carbon was 2.605 ppm less than that of the Cu-(TAC) composite with an adsorbed amount of 6.384 ppm. This is because the adsorbate may still react with the pores of the adsorbent, then when the adsorption time increases, the adsorbate reacts with Cu-(TAC) in the adsorbent. When compared with all time variations of activated carbon with Cu-(TAC) composite, it can be seen that Cu-(TAC) absorbs more β-carotene than activated carbon.

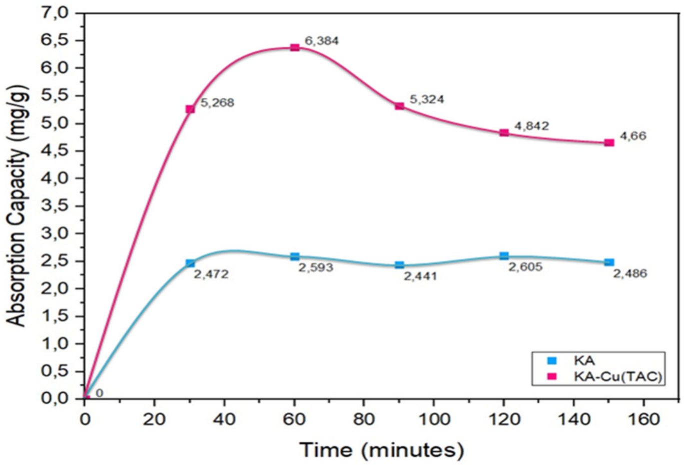


Figure 10. Time Variation of β-Carotene Adsorption Absorption Capacity

The adsorption of the dye solution will decrease when the optimal contact time is reached. This phenomenon occurs because when the optimal contact time is reached, the pores of the adsorbent are filled with adsorbed dye molecules, and the active sites on the surface of the adsorbent become unavailable resulting in desorption. This causes the formation of a new layer on the surface of the adsorbent [8].

3.3 β-carotene desorption

Crude Palm Oil (CPO) is rich in β-carotene, but this adsorption process reduces its content. This is due to the loss of some β-carotene in CPO after adsorption. Desorption is needed, namely the addition of β-carotene extract to CPO after adsorption into activated carbon and Cu-(TAC) composites to increase the β-carotene content and improve the quality of CPO.

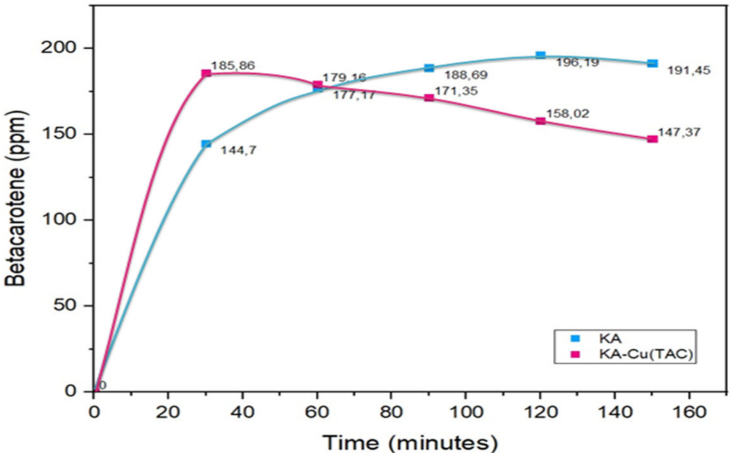


Figure 11. β-carotene desorption

In Figure 3.11 it can be seen that the highest level of β-carotene adsorbed on activated carbon was at 120 minutes, namely 195.19 ppm and at 30 minutes, namely 185.86 ppm in the Cu-(TAC) composite. However, the levels of β-carotene which cannot be released by activated carbon are higher than the levels of β-carotene which cannot be released by the Cu-(TAC) composite.

The desorption percentage indicates how efficiently isopropanol can be used to desorb β-carotene compounds in CPO from activated carbon and Cu-(TAC) composites. To determine the desorption percentage of activated carbon and Cu-(TAC) composites, it can be seen in the following figure.

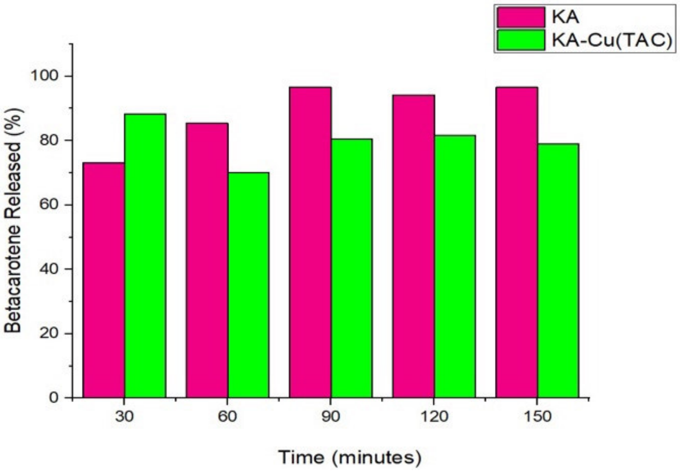


Figure 12. Desorption Percentage of β-Carotene from Active Carbon and Composite Cu(TAC)

Figure 3.12. It can be seen that isopropanol can desorb β-carotene from activated carbon in 150 minutes with 96.252%. In the Cu-(TAC) composite, the highest percentage of β-carotene that could be desorbed was 88.188% in 30 minutes. In other words, it is more difficult for isopropanol to desorb β-carotene contained in the Cu-(TAC) composite because On activated carbon there was a significant increase in the percentage of adsorption. The increase in the percentage of desorption was due to the increase in adsorption power which was accompanied by an increase in the mass of the adsorbent [1].

4. CONCLUSION

The results of the XRD characterization show that activated carbon has an amorphous structure, while the Cu-(TAC) MOFs and Cu-(TAC) composites have a crystalline material structure. Characterization based on SEM at 4000x magnification shows that the Cu-(TAC) composite has pores with smaller cavities than activated carbon. The EDX characterization showed the presence of cu content in Cu-(TAC) MOFs and Cu-(TAC) composites but in very small amounts. BET characterization of activated carbon and Cu-(TAC) composites conforms to the type III isotherm curve and is mesoporous in size.

The optimum condition for using activated carbon in the β-carotene adsorption process is the mass variation of 8 grams with a 0.495 ppm β-carotene content and a contact time of 120 minutes with a 2.605 ppm β-carotene content. The optimum condition for the Cu-(TAC) composite in the β-carotene adsorption process was at 4 gram mass variation with 1.026 ppm of β-carotene and contact time at 60 minutes with 6.384 ppm of β-carotene. This shows that the adsorption ability of the Cu-(TAC) composite is better than activated carbon in adsorbing β-carotene.

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