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Synthesis and Characterization of UiO-66 as a Paracetamol Absorption Material

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***Abstract**: UiO-66 synthesis has been carried out by dissolving 0.53 grams of zirconium tetrachloride (ZrCl4) and 0.34 grams of Benzene-1,4-dicarboxylic Acid (H2BDC) in 30 mL Dimethylformamide (DMF). The solution is then distilled for 30 minutes and then heated in an oven at 140 ° C for 6 hours. The UiO-66 material produced was then characterized by an X-Ray Diffractometer (XRD) and Fourier Transform Infrared (FTIR). The results showed that the UiO-66 was successfully synthesized which supported the XRD results at 2θ 7.3o, 8.49o and 25.8o which were the peak characteristics of UiO-66. In addition, the FTIR results show a peak of around 1500 cm-1 showing vibrations of C = C on the benzene ring and a peak of about 1390 cm-1 indicating streching of O-C-O produced from the ligand. The peaks are around 750, and 660 cm-1 which indicates the presence of C-H vibrations from the ligand. UiO-66 was also approved as the adsorption agent of paracetamol which was approved with the highest adsorption of paracetamol at 72 hours soaking time which was 97.03%.*

Keywords: *Synthesis, UiO-66, Paracetamol, Adsorption*

1. INTRODUCTION

Metal-Organic Framework (MOF) or also called porous coordination polymer is a material formed between a combination of metals and ligand. MOF is a new material that has the potential to be developed because it has a pore which is creepy, a large area, and high adsorption power (Cavka et al. 2008). This has caused MOF to be widely used in various fields, including separation, adsorption, electrochemical, catalyst and drug delivery (Roswell et al., (2004); Xamena et al. (2007); Couck et al. (2009)). On the other hand, MOF also has advantages compared to other conventional materials, its structure can be modified depending on its use. Some MOFs have been synthesized by modifying central metals and ligand among IRMOF (Isoreticular Metal-Organic Framework), ZIF (Zeolite Imidazole Framework), HKUST (Hong Kong University of Science and Technology) and UiO-66 (University of Oslo) (Rahmawati, et al. (Rahmawati, et al.) 2014)).

UiO-66 is a type of MOF formed from zirconium metal ion (Zr4 +) and terephthalic acid ligand (BDC) where each Zr atom coordinates with eight oxygen

atoms to form an antiprismatic cube. The advantage of UiO-66 compared to other types of MOF is its high structural stability so that it is easy to synthesize and can be applied to various fields. Several studies for the synthesis of UiO-66 have been carried out. Zhao, et al. (2014) synthesized UiO-66 at 120oC for 16 hours. Cavka, et al. (2008) and Abid, et al. (2012) synthesized UiO-66 at 120oC for 24 hours. Research Rahmawati, et al. (2014) showed that UiO-66 was successfully synthesized by the solvothermal method at 140oC with an optimum time of 6 hours. On the other hand, UiO-66 has also been applied in various fields.

Abid, et al. (2012) applied UiO-66 as a storage material for hydrogen and carbon dioxide gas. Zhao, et al. (2017) applied UiO-66 as a stationary phase of HPLC for the separation of Benzene and polycyclic hydrocarbons. Masoomi, et al. (2016) applied UiO-66 to adsorb Kongo red dyes in water. On the other hand, UiO-66 is also applied as a drug delivery agent because of its low toxicity and high chemical stability. Mocniak, et al. (2015) applied UiO-66 for the introduction of the drug cisplatin. Research by Rojas, et al. (2018) showed that UiO-66 for aspirin and ibuprofen was the most effective drug compared to MIL-100 and MIL-127. On the other hand, the research application of UiO-66 as an adsorbent of paracetamol has never been done.

Paracetamol is a type of drug used to relieve fever. Usually, paracetamol is consumed every 4 hours. On the other hand, paracetamol can cause liver damage when consumed in high concentrations (Wiratama, et al., 2017), so we need a material that can deliver paracetamol properly. Besides that, paracetamol is also often found in the aquatic phase, so that it can be a source of pollutants in water (Desale, et al., 2013).

Based on the above background, the synthesis and characterization of UiO-66 as the adsorbing material for paracetamol was carried out in this study. The purpose of this study is to look at the ability of UiO-66 as an adsorbent of paracetamol so that it can be seen the potential of UiO-66 as a micropollutant model in water (Schelling, et al. (2018) and as a drug delivery model (Tai, et al., 2016).

2. METHOD

Instrumentation

The instrumentation needed in this study are glassware, analytical balance for weighing materials, closed vials for reaction, ovens for synthesis, UV-VIS, X-ray Diffractophotometer (XRD-JEOL), and Fourier Transform Infrared (FTIR-Shimadzu).

Material

Materials needed in this study are zirconium tetrachloride ($ZrCl_4$), Benzene-1,4-dicarboxylic acid (H_2BDC), Dimethylformamide (DMF), chloroform, methanol, paracetamol, and aquadest

Synthesis of UiO-66

The making of UiO-66 was done by modifying Rahmawati et al. with dissolving 0.53 grams of zirconium tetrachloride ($ZrCl_4$) and 0.34 grams of Benzene-1,4-dicarboxylic acid (H_2BDC) in 30 ml Dimethylformamide (DMF). The solution is then distilled for 30 minutes and then heated in an oven at 140 ° C for 6 hours. The result cools at room temperature until overnight. The solution is then decanted, the solid is washed with 30 mL DMF and then left overnight. The solid is washed again with 30 ml chloroform twice. The results of the solids that have been washed, then dried in 65°C for 24 hours to obtain the solid UiO-66 (uio).

The characterization of UiO-66

The UiO-66 material is characterized by its crystalline structure with an X-Ray Diffractometer (XRD) and its functional group with Fourier Transform Infrared (FTIR).

Adsorption Ability of UiO-66 to Paracetamol

The application of adsorption on paracetamol was carried out by dispersing 0.2 grams of UiO-66 in 10 mL of methanol and adding 10 mL of paracetamol (1000 mg / L). The mixture is stirred at room temperature for 12, 24, 36, 48, and 72 hours. The results were centrifuged and washed with water, then measured levels of paracetamol adsorbed with UV-Vis at a wavelength of 249 nm. The solid application results are then dried and characterized by XRD and FTIR (uiop).

UiO-66 stability test in the process of Paracetamol Adsorption

UiO-66 stability test in the paracetamol adsorption process was carried out by comparing FTIR spectra and UiO-66 diffractogram pattern before and after the process of adsorption of paracetamol.

3. RESULT AND DISCUSSION

Synthesis of UiO-66

Synthesis of UiO-66 was carried out by dissolving 0.53 grams of zirconium tetrachloride ($ZrCl_4$) and 0.34 Benzene-1,4-dicarboxylic acid (H_2BDC) in Dimethylformamide (DMF) then heated at 140 °C for 6 hours. The use of temperature and duration of the heating is based on research by Rahmawati et al. (2014) because at these temperatures the formation of UiO-66 with the best characteristics (crystallinity, stability and pore structure). Before heating, a solution of a mixture of $ZrCl_4$, H_2BDC and DMF is clear, then after heating it forms a mixture of clear liquid and white solid.

Then, the mixture is separated and the solid is washed with DMF to remove any remaining unreacted compounds. After washing with DMF, the solid is then washed again with chloroform to remove residual DMF (Abid et al., 2012). The solid is then heated at 65 °C to remove chloroform, the selection of the heating temperature is based on the boiling point of the chloroform which is 61.2 °C (Rahmawati, et al., 2014). After drying, white UiO-66 powder is formed.

The characterization of UiO-66

The characterization of UiO-66 was carried out to prove that the solid UiO-66 has been successfully formed. In this study, the formation of UiO-66 was proven by the XRD diffractogram pattern (Figure 1a) and FTIR spectra (Figure 1b).

The determination of the crystallinity of the sample was determined by X-Ray Diffraction (XRD) at 2θ at 5°-70°. Figure 1a. showed that the characterization of UiO-66 with XRD showed the presence of 3 characteristic peaks at 2θ 7.3° and 8.49° according to the study of Zhao, et al. (2013) and Rahmawati, et al. (2014). This shows that the presence of a sharp peak in the XRD pattern of the sample indicates that a good level of crystallinity of the synthesized UiO-66 product. To confirm these results, characterization was carried out with Fourier Transform Infrared (FTIR) (Figure 1b).

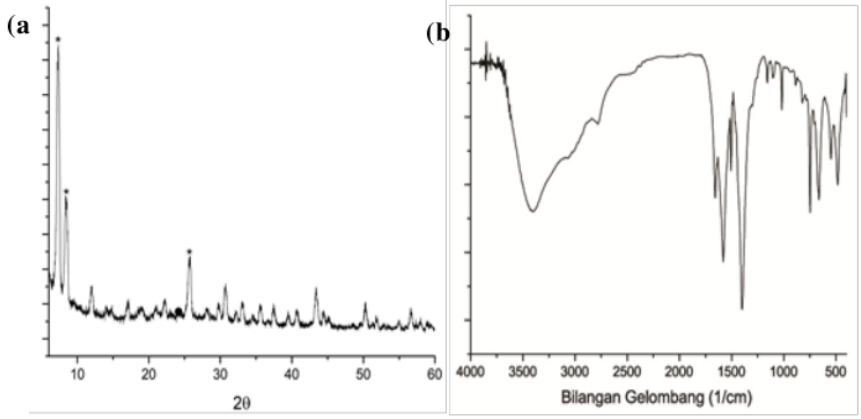

Figure 1. The characterization of UiO-66 **(a)** Difraktogram XRD **(b)** Spektra

Characterization with FTIR (Figure 1b) aims to determine the functional group of UiO-66. The results of the UiO-66 characteristics are consistent with the research of Kandiah et al. (2010) and Schelling, et al. (2018). The peaks around 1570 cm-1 indicate a reaction between -COOH dicarboxylic benzene acid which is a ligand that reacts with Zr^{4+} as the central metal in the synthesis of UiO-66. On the other hand, peaks around 1500 cm-1 show vibrations of C = C on the benzene ring and peaks around 1390 cm-1 which indicate stretching of O-C-O originating from ligands. The peaks are around 750, and 660 cm-1 which indicates the presence of C-H vibrations from the ligand. These results indicate that UiO-66 has been successfully synthesized.

Adsorption Ability of UiO-66 to Paracetamol

The application of UiO-66 for adsorption of paracetamol is shown in Table 1. The adsorption of paracetamol was carried out by mixing 0.2 grams of UiO-66

in 10 mL methanol and adding 10 mL of paracetamol solution (1000 mg / L). The mixture is stirred at room temperature for 12, 24, 36, 48, and 72 hours. The results obtained were then tested by UV-Vis with a wavelength of 249 nm. The highest adsorption at the 72 hour soaking time is 97.03%.

Table 1 shows that the longer the soaking time the greater the paracetamol adsorbed. These results are consistent with the research of Li, et al., (2015) which shows that the greater the soaking time, the 5-Fluorouracil concentration decreases. Table 1 also shows that the adsorption of UiO-66 in paracetamol is greater (97.03%) compared to the adsorption of paracetamol with other studies, such as in Chang, et al. (2015) which showed that the adsorption of paracetamol with ZSM-5 material reached 96.6%, while in the study of Ilomuanya, et al. (2017) showed that the adsorption of paracetamol with activated carbon adsorbents only reached 95%.

Tabel 1. Paracetamol adsorption in UiO-66 at various soaking times

Soaking Time (h)	Concentration of Residual Paracetamol (ppm)	Concentration of adsorbed paracetamol (ppm)	Adsorbed paracetamol (%)
12	37,39	962,61	96,26
24	34,31	965,69	96,57
36	33,41	966, 59	96,66
48	32,13	967,87	96,79
72	29,70	970,30	97,03

UiO-66 stability test in the process of Paracetamol Adsorption

XRD analysis

A comparison of the UiO-66 diffractogram pattern before and after the adsorption process of paracetamol is shown in Figure 2. The diffractogram pattern before the adsorption process (uio) did not change significantly after the adsorption process (uiop). Figure 2 shows that the paracetamol adsorption process did not affect the crystal structure of UiO-66 (Li, et al., 2019). This result also shows that UiO-66 has high chemical stability. Rojas, et al. (2018), making it suitable for use as a micropolutan model in water or as a drug delivery model.

Based on Figure 2, the peak characteristic of UiO-66 both before and after adsorption of paracetamol is still sharp, at 7.3°; 8.49°. On the other hand, at a peak of 8.49°, it decreases with increasing the soaking time. This shows that paracetamol has been adsorbed in the pore of UiO-66. This is in accordance with the results of the study of Tai, et al., (2016) which shows that the peak characteristic of UiO-66 will decrease with increasing soaking time 5-Fluorouracil (5-Fu).

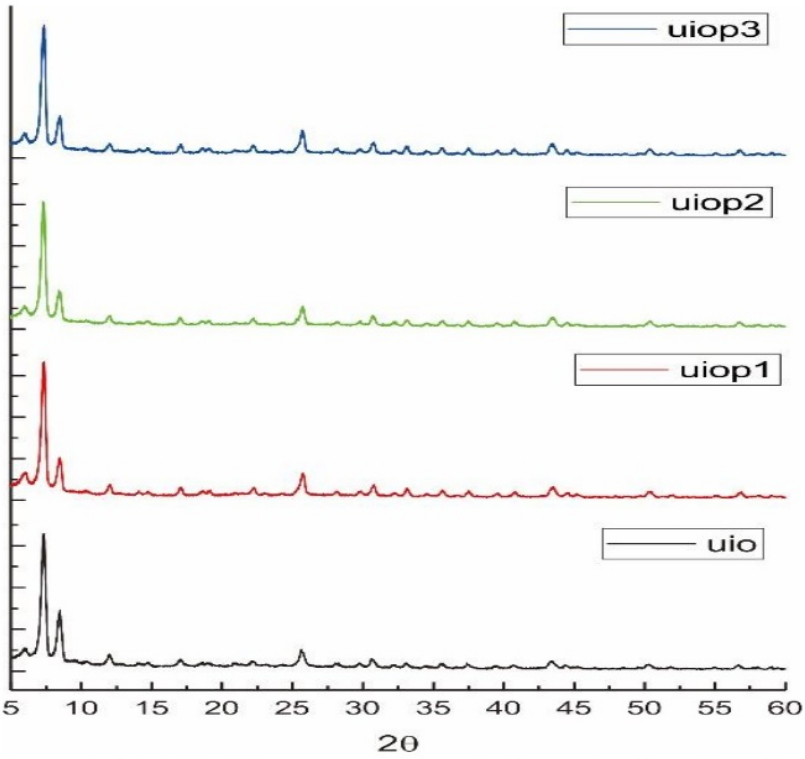

Figure 2. UiO-66 diffractogram pattern before and after adsorption of paracetamol: uio: UiO-66; uiop1: UiO-66 adsorption of paracetamol for 1 hour; uiop2: UiO-66 adsorption of paracetamol for 2 hours; uiop3: UiO-66 adsorption of paracetamol for 3 hours.

FTIR analysis

A comparison of FTIR UiO-66 spectra before and after the adsorption process of paracetamol is shown in Figure 3. Based on Figure 3, the FTIR UiO-66 spectra before the adsorption process (uio) did not change significantly with the FTIR spectra UiO-66 after the adsorption process (uiop). The FTIR spectra in Figure 3 also increasingly prove that UiO-66 has high chemical stability.

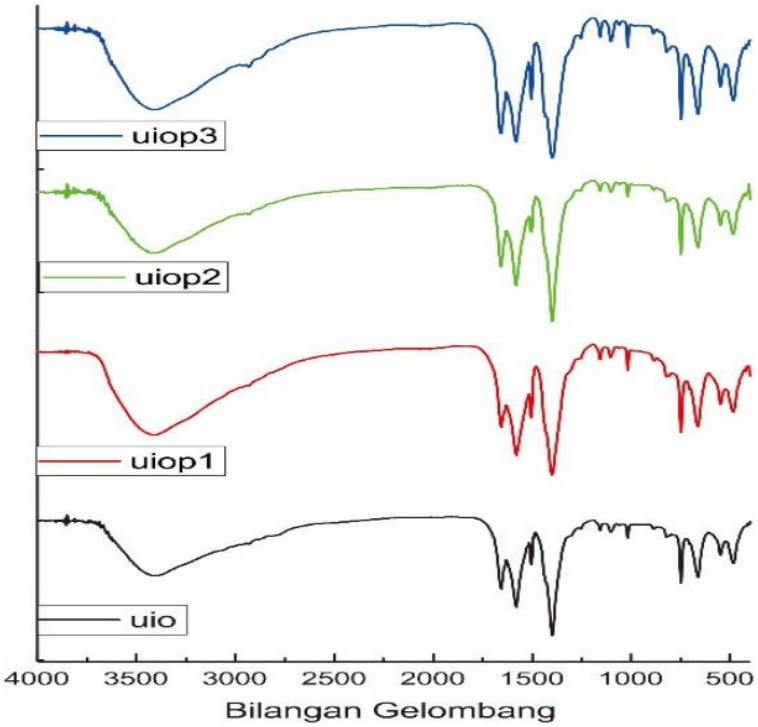

Figure 3. FTIR spectra of UiO-66 before and after adsorption of paracetamol: uio: UiO-66; uiop1: UiO-66 adsorption of paracetamol for 1 hour; uiop2: UiO-66 adsorption of paracetamol for 2 hours; uiop3: UiO-66 adsorption of paracetamol for 3 hours.

Based on Figure 3, it shows that at a wavelength of 1658 cm-1 there is an increase in intensity in line with the length of time of adsorption of paracetamol which indicates the presence of C = O groups from paracetamol. This is consistent with the study of Trivedi, et al (2015) which showed an increase in intensity at a wavelength of 1658 cm^{-1}. These results indicate that paracetamol was successfully adsorbed on the surface of UiO-66. On the other hand, the characteristic peak of UiO-66 is that the wavenumber 1570 cm^{-1} is still present, so this result shows the high chemical stability of UiO-66 (Li, et al. 2019).

4. CONCLUSION

The results showed that UiO-66 was successfully synthesized as indicated by the XRD results at 7.3°, 8.49°, and 25.8° which were the peak characteristics of UiO-66. Besides that, the FTIR results show a peak around 1570 cm^{-1} indicates a reaction between –COOH and Zr^{4+}; 1500 cm^{-1} shows the vibrations of C = C on the benzene ring and the peak around 1390 cm^{-1} which shows the stretching of O-C-O originating from the ligand. The peaks are around 750, and 660 cm-1 which indicates the presence of C-H vibrations from the ligand. UiO-66 also has the potential as a paracetamol adsorption material as indicated by the highest adsorption of paracetamol at 72 hours immersion time which is 97.03%.

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