

## INFLUENCE OF SOLVOTHERMAL TEMPERATURES AND TIMES ON CRYSTALLINITY AND MORPHOLOGY OF MOF-5

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### ABSTRACT

MOF-5 (metal-organic frameworks-5) have been synthesized using solvothermal method in which reaction mixtures of zinc nitrate hexahydrate and 1,4-benzenedicarboxylic acid (BDC) in dimethylformamide (DMF) were heated at various heating temperatures and times in order to observe the influence of heating temperature and time on crystallinity and morphology of the obtained MOF-5. The heating temperatures used were 105, 120 and 140 °C, respectively with heating times of 12–144 h. Determination of the best reaction conditions was based on the observation of phase purity and crystal morphology of MOF-5 using XRD and SEM. The characterization results showed that MOF-5 crystals with a higher crystallinity were obtained when the reaction mixtures were heated at 105 °C for 144 h, 120 °C for 24 h or 140 °C for 12 h. The maximum weight of MOF-5 crystal was generated from reaction mixture heated at 120 °C for 72 h.

**Keywords:** MOF-5; solvothermal; synthesis; crystallinity; morphology

### ABSTRAK

MOF-5 (metal-organic frameworks-5) telah disintesis dengan metode solvotermal melalui pelarutan seng nitrat heksahidrat dan asam 1,4-benzendikarboksilat (BDC) dalam dimetilformamida (DMF), dilanjutkan dengan pemanasan pada berbagai suhu dan waktu, untuk mengamati pengaruh suhu dan waktu pemanasan terhadap kristalinitas dan morfologi MOF-5 yang dihasilkan. Suhu pemanasan yang digunakan berturut-turut adalah 105, 120 dan 140 °C, dengan waktu pemanasan 12–144 jam. Penentuan kondisi reaksi terbaik didasarkan pada pengamatan terhadap kemurnian fasa dan morfologi MOF-5 menggunakan XRD dan SEM. Hasil karakterisasi menunjukkan bahwa MOF-5 dengan kristalinitas lebih tinggi dapat dihasilkan dari campuran reaksi yang dipanaskan pada suhu 105 °C selama 144 jam, 120 °C selama 24 jam dan 140 °C selama 12 jam. Berat kristal MOF-5 maksimum dihasilkan dari campuran reaksi yang dipanaskan pada suhu 120 °C selama 72 jam.

**Kata Kunci:** MOF-5; solvotermal; sintesis; kristalinitas; morfologi

### INTRODUCTION

Metal-organic frameworks (MOFs) are new type materials in which the metal ion acts as a coordinating centre and associated with a variety of polyatomic organic compounds to form three-dimensional structures. By changing the metal ions and ligands used, materials with variety in porosity, surface area and pore size can be obtained [1]. One type of MOFs which is still intensively investigated to date is MOF-5. The advantages of MOF-5 include a large surface area, high porosity and low-cost and readily available raw materials [2]. MOF-5, with molecular formula of  $Zn_4O(BDC)_3$ , has been synthesized from  $Zn(NO_3)_2 \cdot 6H_2O$  (zinc nitrate hexahydrate) as the inorganic material associated with  $H_2BDC$  (1,4-benzene dicarboxylic acid) as the organic linker and DEF (*N,N*-diethylformamide) or DMF (*N,N*-dimethylformamide) as solvents. The DEF is preferred

as a reaction solvent even though the DMF can be used as a substitute for the equivalent phase but get lower quality and cheaper price [3].

Methods for MOF-5 synthesis have been developed with the aim of obtaining materials with high surface area and pore volume. It has been reported that MOF-5 has been synthesized by use of solvothermal method as well as sonochemical [4] and microwave methods [3]. Solvothermal method is widely used as MOF-5 crystals with high crystallinity, large surface area and pore volume have been produced [5]. The parameters influenced the characteristics of MOF-5 crystals depend on reaction parameters such as reaction temperature, reaction time, ratio of metal/ligand, solvent composition and pH of the solution [6].

Some researchers have reported the synthesis and characterization of MOF-5 by use of the

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solvothermal method at various reaction conditions. Biemmi et al. [7] have synthesized MOF-5 at 110 °C for 48 h and the product has a typical diffractogram pattern of MOF-5. Lu et al. [8] and Son et al. [4] have reported that MOF-5 crystals with a surface area of 1080 and 3200 m<sup>2</sup>/g have been obtained at a heating temperature of 105 °C for 20 and 24 h, respectively. Furthermore, Phan et al. [9] and Blanita et al. [2] have shown that higher surface area and pore diameter of MOF-5, i.e. 3846 m<sup>2</sup>/g and 18.6 Å as well as 3153 m<sup>2</sup>/g and 18.3 Å, have been synthesized at 100 °C for 7 and 24 h, respectively. In addition, Zhao et al. [10] have also reported the synthesis of MOF-5 at 130 °C for 4 h which produces cubic crystals. The results mentioned above indicate that the heating temperature and time in the synthesis of MOF-5 can affect the characteristics of the obtained MOF-5. Therefore, research on the optimization of reaction conditions for synthesis of MOF-5 in order to obtain MOF-5 crystals with the desired characteristics is still required.

Several studies conducted by Orefuwa et al. [11], Venna et al. [12], and Biemmi et al. [7] have discussed the optimization of reaction temperatures and times for the synthesis of MOFs. Orefuwa et al. [11] have reported the effect of reaction temperatures on the structure of IRMOF-8 in which an intermediate phase and other products have been formed when the reaction temperatures of 100 and 150 °C were used. An evolution of ZIF-8 structure as a function of times has been reported by Venna et al. [12], i.e. the phase purity of ZIF-8 increased with the increase in reaction time and remained unchanged after 50 min, whereas the particle size of ZIF-8 increased with the increase in reaction time. The research results of Biemmi et al. [7] have shown the evolution of the HKUST-1 structure as a function of temperature despite the formation of metal oxide, Cu<sub>2</sub>O, phase at a temperature of 180 °C. In addition, the regularity of morphology of the HKUST-1 crystals decreased with the increase in reaction temperatures. In the case of MOF-5 synthesis, Choi et al. [13] have investigated the effect of reaction time on crystallinity of MOF-5 synthesized by use of microwave method at various reaction time of 15, 30, 45 and 60 min. Diffractogram patterns of MOF-5 generated from reaction time of 15, 45, and 60 min showed the highest peak intensity at 2θ of 9.6 and 6.8° when the reaction time was 30 min.

In this work, synthesis of MOF-5 by use of solvothermal methods at various heating temperatures of 105, 120 and 140 °C, for various heating times of 12, 24, 36, 48, 72 and 144 h have been performed. Determination of the best reaction conditions for the synthesis of MOF-5 has been focused on the observation of phase purity and crystal morphology of

MOF-5 through characterization results by XRD and SEM.

## EXPERIMENTAL SECTION

### Materials

Both reactants of zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and 1,4-benzenedicarboxylic acid (H<sub>2</sub>BDC) with purity of 99.0% were supplied by Sigma-Aldrich, while solvents of N,N-dimethylformamide (DMF) with purity of 99.8% and chloroform (CHCl<sub>3</sub>) with purity of 99.9% were supplied by Merck and used as received. The ultra-high purity of nitrogen gas was purchased from Samator Gas.

### Instrumentation

The crystalline structures of the obtained samples were determined by X-ray diffraction (XRD) by use of a JEOL diffractometer with a Cu Kα radiation (λ = 1.54056 Å) at 40 kV and 30 mA. The diffractogram were recorded with a 2θ scale of 5–50° and a scan speed of 0.020°/sec. IR spectra were recorded on a Bruker FT-IR spectrometer between 400–4000 cm<sup>-1</sup> at room temperature with the sample scan time was 32 sec. Surface morphology and estimated particle size were observed using Scanning Electron Microscopy (Zeiss EVO MA10). The percentage of elements in the crystals was estimated by SEM-EDX.

### Procedure

#### Synthesis of MOF-5

The synthesis of MOF-5 has been carried out by dissolving 6.48 g of zinc nitrate hexahydrate (6.1 mmol) and 1.188 g of 1,4-benzenedicarboxylic acid (2.0 mmol) in 180 mL DMF, then stirred with magnetic stirrer for 30 min. The reaction mixture was then transferred into 6 of 50 mL vial botols with lids, each with a volume of 30 mL, and heated in an oven at 105 °C. Each reaction mixture was taken out from the oven at intervals of 12, 24, 36, 48, 72 and 144 h, allowed to cool at room temperature. The solvent was then removed from the vial bottles by decantation, the solid was washed by adding 30 mL of DMF and left for 24 h. The washing process was repeated twice with chloroform. The obtained solid was then dried under vacuum at 60 °C and stored in a container with a nitrogen atmosphere and weighed. The same process was repeated for the heating temperatures of 120 and 140 °C.

## RESULT AND DISCUSSION

### Synthesis of MOF-5

The clear solution of  $Zn(NO_3)_2 \cdot 6H_2O$  and  $H_2BDC$  in DMF (Fig. 1a) turned into a mixture of white solid on the walls and bottom of the vial bottle, and clear filtrate (Fig. 1b), after the heating process. After washing and drying process, the white crystals were obtained (Fig. 1c).

The weight of the crystals produced at each heating temperature is shown in Fig. 2. At a temperature of 105 °C, the weight of the resulting crystals increases with the increase in heating time to reach a maximum of 0.53 g after heating for 144 h. At the reaction conditions of 120 °C for 72 h and 140 °C for 36 h, however, the weight of the obtained crystals were as much as 0.68 and 0.61 g, respectively. The reaction condition that produced crystal highest weight was heating at a temperature of 120 °C for 72 h (Fig. 2).

### Characteristics of MOF-5

Diffraction pattern of crystals synthesized at 105 °C for 12–144 h and simulated diffraction pattern of MOF-5 are shown in Fig. 3. As is shown in the Fig. 3, crystals obtained at heating time for 12 h (a) has different diffraction pattern to that of simulated MOF-5 which indicates that MOF-5 crystal has not been formed. When the heating times were increased up to 36 h, the MOF-5 crystals have been formed along with the presence of impurities, as indicated from the appearance

of small peak at  $2\theta = 6.8^\circ$  on the diffractogram b and c. Further increase in the heating time for 48–144 h resulted in the formation of crystals with the same

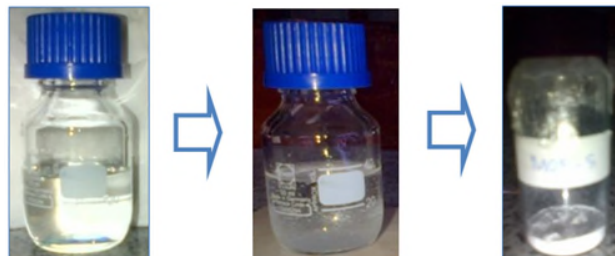


Fig 1. The synthesis process of MOF-5

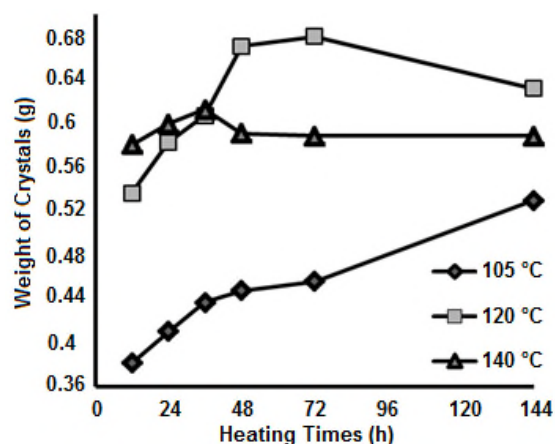


Fig 2. Weight of crystals at various solvothermal temperatures and times

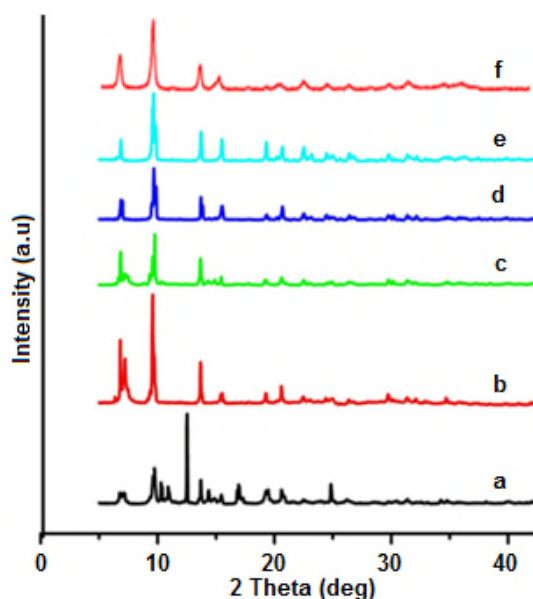


Fig 3. Diffraction patterns of crystals obtained at 105 °C for: a. 12 h, b. 24 h, c. 36 h, d. 48 h, e. 144 h, f. Simulated of MOF-5

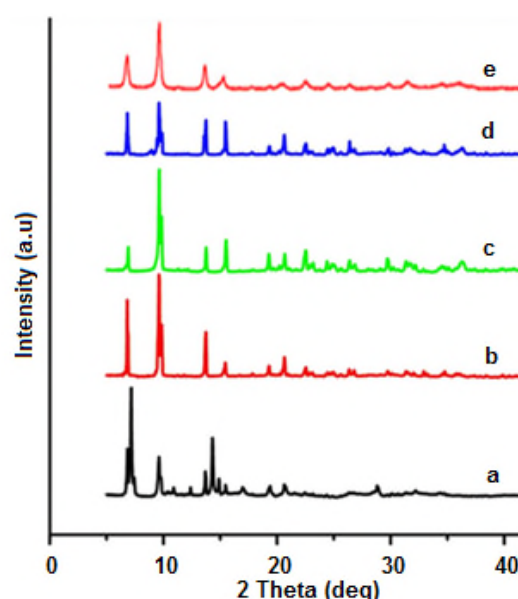
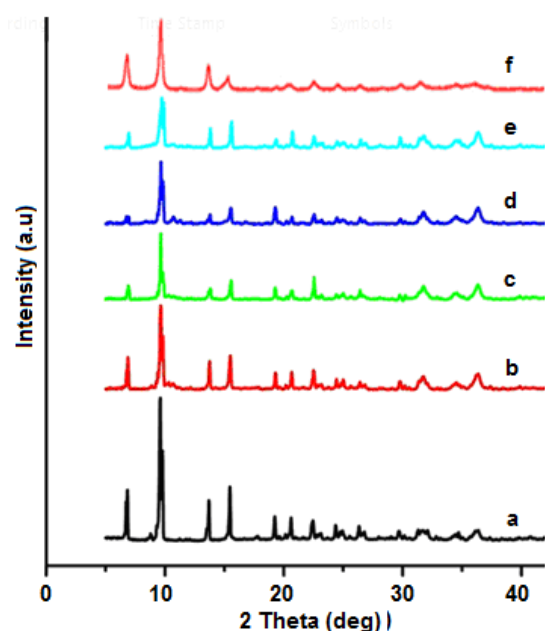


Fig 4. Diffraction patterns of crystals obtained at 120 °C for: a. 12 h, b. 24 h, c. 48 h, d. 144 h, e. Simulated of MOF-5



**Fig 5.** Diffraction patterns of crystals obtained at 140 °C for: a. 12 h, b. 24 h, c. 36 h, d. 72 h, e. 144 h, f. Simulated of MOF-5

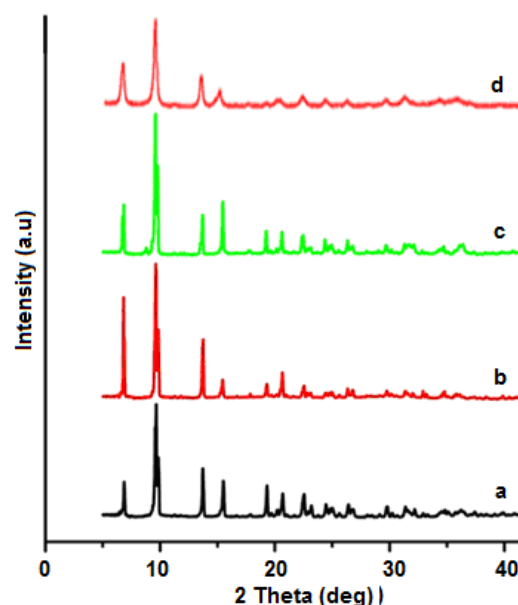
**Table 1.** Peak area and crystallinity of MOF-5 at optimum reaction conditions

Crystal	Synthesis Conditions	Peak Area (unit)	Crystallinity (%)
A	105°C-144 h	4940	91
B	120°C-24 h	5406	100
C	140°C-12 h	3840	71

diffraction patterns to that of simulated MOF-5 (Fig. 3f). The formation of MOF-5 is indicated by the presence of four peaks at  $2\theta = 6.8; 9.6; 13.7$  and  $15.4^\circ$  (Fig. 3f) as reported by Li et al. [5]. The highest crystal weight of 0.530 g has been achieved by heating time for 144 h.

Diffraction pattern of crystals synthesized at 120 °C for 12–144 h and the simulated diffraction pattern of MOF-5 are shown in Fig. 4. At the heating temperature of 120 °C, MOF-5 crystals have formed after reaction times of 24 h as indicated by the appearance of peaks characteristic to MOF-5 at  $2\theta = 6.8; 9.6; 13.7$  and  $15.4^\circ$ . As can be seen in Fig. 4b, c and d, the crystals obtained with heating times of 24–144 h show the same diffraction pattern to that of simulated MOF-5 (Fig. 4e) [5]. The intensity of the four main peaks, however, decreases with the increase in heating time, which indicates that the crystallinity of the MOF-5 decreases with the increase in heating time. Based on these results, the best heating time at 120 °C was 24 h.

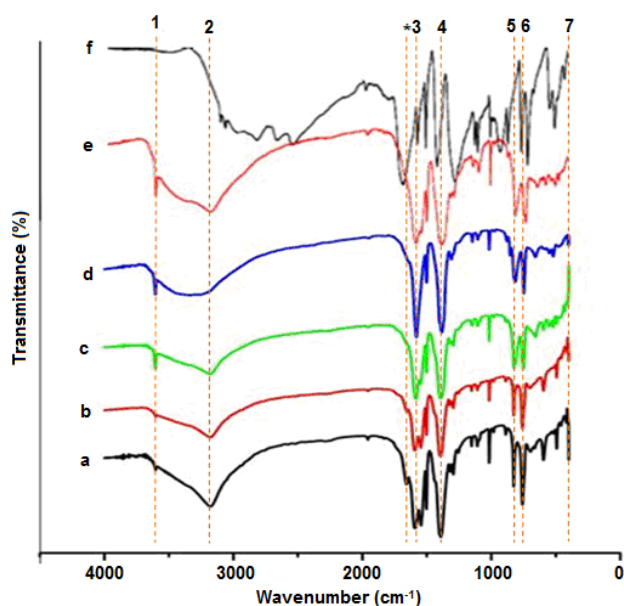
Diffraction pattern of crystals synthesized at 140 °C for 12–144 h and the simulated diffraction pattern of MOF-5 are shown in Fig. 5. As indicated in Fig. 5, the crystal obtained at heating temperature of 140 °C for 12



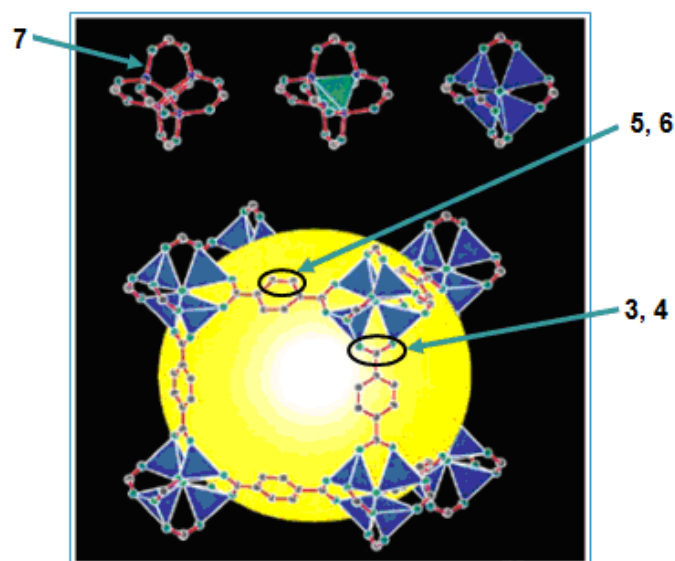
**Fig 6.** Diffraction Patterns of MOF-5 synthesized at: a. 105 °C for 144 h, b. 120 °C for 48 h, c. 140 °C for 12 h, d. Simulated of MOF-5

h shows the peak of the simulated MOF-5, i.e. at  $2\theta = 6.8; 9.6; 13.7$  and  $15.4^\circ$ . The characteristic peaks of the MOF-5 still appear on the diffractogram of crystals synthesized at 140 °C for 24 – 144 h, even though the intensity of the peaks decrease with the increase in heating time (Fig. 5b-5e). Therefore, based on the crystallinity of the obtained crystals, the best solvothermal time for synthesis of MOF-5 at a temperature of 140 °C is 12 h.

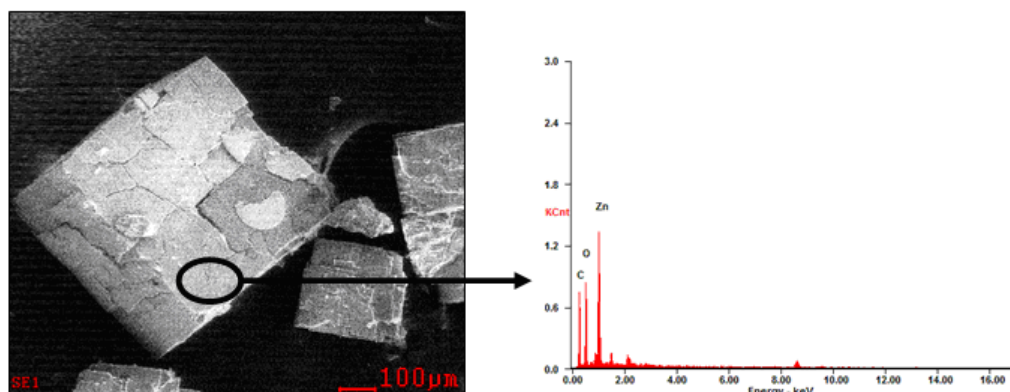
As explained, the best solvothermal conditions for the synthesis of MOF-5 are 105 °C - 144 h, 120 °C - 24 h and 140 °C - 12 h. The conditions have been chosen as the resulting diffractogram patterns of the crystals follow the pattern of simulated diffractogram of MOF-5 and have highest crystallinity. Nevertheless, from a comparison of the diffractogram of the three selected crystals and simulated of MOF-5 (Fig. 6), it is seen that the crystal obtained at 120 °C for 24 h has the same pattern to the simulated diffractogram of MOF-5 (Fig. 6b and d). The crystallinity of each diffractogram pattern has been calculated based on the four main peak areas of MOF-5 characteristics, analogy to the calculation of peak area carried out by Jiang et al. [17]. Crystal with the largest peak area, expressed as 100% crystallinity, whereas the crystallinity of other crystals with lower peak area, is calculated relative to the peak area of the highest value. The crystallinity calculation results are shown in Table 1. Crystal with the highest crystallinity was obtained from the solvothermal condition of 120 °C for 24 h.



**Fig 7.** FTIR spectra of MOF-5 synthesized at: a. 105 °C for 144 h, b. 120 °C for 48 h, c. 140 °C for 12 h, d. simulated of MOF-5, e. reported for MOF-5



**Fig 8.** Diffraction patterns of MOF-5 synthesized at: a. 105 °C for 144 h, b. 120 °C for 48 h, c. 140 °C for 12 h, d. Simulated of MOF-5



**Fig 9.** SEM-EDX images of MOF-5 synthesized at 105 °C for 144 h

The FTIR spectra of the obtained MOF-5 with high crystallinity as well as the FTIR spectra of the H<sub>2</sub>BDC ligand and the reported for MOF-5 are shown in Fig. 7, while the chemical bond structure corresponding to that reported for MOF-5 is shown in Fig. 8. As are shown in Fig. 7 and 8, the main bond connectivity in the motif of MOF-5 structure is associated with the main FTIR band observed. The two vibration bands located at 1593 cm<sup>-1</sup> and 1387 cm<sup>-1</sup> with strong intensity are due to the carboxylic (COO) asymmetric stretching and symmetric stretching vibrations, respectively. The absorption peak at 459 cm<sup>-1</sup> is relevant to the secondary building unit (SBU) of MOF-5, which represents the Zn-O stretching vibration of tetrahedral coordinated Zn<sub>4</sub>O cluster [18-19]. Two sharp peaks observed at 827 cm<sup>-1</sup> and 759 cm<sup>-1</sup> are related to the presence of the C-H group in the benzene ring of terephthalic acid [19]. Broad absorption band in

the 3200-3500 cm<sup>-1</sup> frequency region indicates the presence of adsorbed water [8,19].

The crystal morphology of MOF-5 and the approximate elemental composition observed using SEM-EDX are shown in Fig. 9–11. As can be seen from the SEM photographs, the morphology of MOF-5 crystals obtained in this study is in accordance to the SEM photograph of MOF-5 reported by Li et al. [5]. The three MOF-5 crystals obtained in this study show morphologies of cube with various surface textures. As can be seen in Fig. 11, a flat smooth surface morphology with smaller particle size (85-95 μm), is shown by the MOF-5 crystal synthesized at a high temperature (140 °C) with a short time (12 h). At lower solvothermal temperatures and longer times, i.e. at 100 °C for 144 h and 120 °C for 24 h, the obtained MOF-5 crystals have larger particle size (250–300 μm),

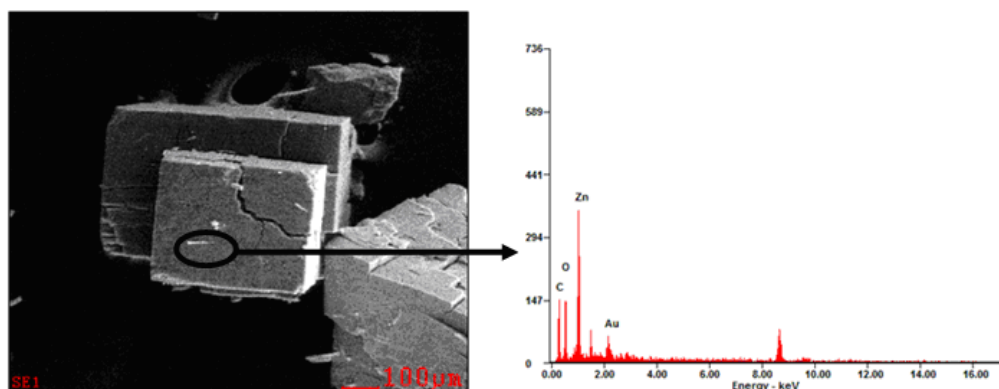


Fig 10. SEM-EDX images of MOF-5 synthesized at 120 °C for 24 h

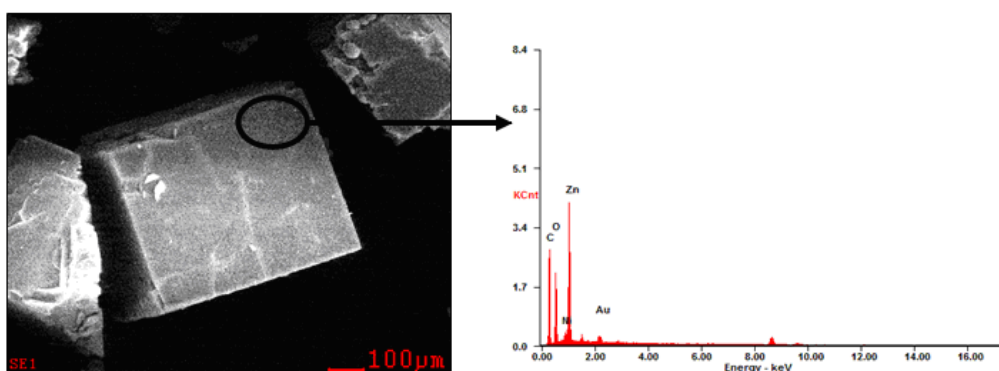


Fig 11. SEM-EDX Images of MOF-5 synthesized at 140 °C for 12 h

as are shown in Fig. 9 and 10. Compared to the results reported by Yang et al. [20], MOF-5 crystals synthesized at 140 °C for 12 h have similar particle size, i.e. 100–110 μm. While the particle size of the crystals synthesized at 100 °C for 144 h and 120 °C for 24 h were similar to those reported by Mueller et al. [21], i.e. 200–250 μm.

Elemental compositions of MOF-5 crystals estimated from the SEM-EDX are shown in Fig. 9–11. Compared to the elemental composition of the simulated MOF-5, crystal obtained with solvothermal temperature of 120 °C for 24 h has very similar to that of the simulated MOF-5 [21]. This suggests that the empirical formula of the MOF-5 obtained in this study may be  $Zn_{4.26}O_{12.8}C_{24}H_{11.3}$  with a structure as is shown in Fig. 8.

## CONCLUSION

Based on the XRD patterns, the optimum solvothermal time at a temperature of 105 °C was 12 h, at a temperature of 120 °C was 48 h, and while at a temperature of 140 °C was 144 h. The SEM results showed that the three solvothermal conditions, i.e. 105 °C for 144 h, 120 °C for 24 h and 140 °C for 12 h, produced MOF-5 with cube morphology. The MOF-5 obtained at solvothermal temperature of 140 °C for 12 h

showed the smoothest surface morphology and the smallest crystal size (85–95 μm). The best reaction condition for synthesis of MOF-5 with high crystallinity is suggested at solvothermal temperature of 120 °C for 24 h.

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