

[fdmp] Submission Acknowledgement

noreply@tspsubmission.com <noreply@tspsubmission.com>

on behalf of

FDMP Editorial <fdmp@techscience.com>

Fri 29/05/2020 11:14

To: Sulardjaka <sulardjaka@lecturer.undip.ac.id>

Sulardjaka Sulardjaka:

Thank you for submitting the manuscript, "Zeolite A Prepared from Geothermal Waste by Microwave-Hydrothermal and Conventional-Hydrothermal" to Fluid Dynamics & Materials Processing. With the online journal management system that we are using, you will be able to track its progress through the editorial process by logging in to the journal web site:

Submission URL: <http://tspsubmission.com/index.php/fdmp/authorDashboard/submission/11784>

Username: sulardjaka

If you have any questions, please contact me. Thank you for considering this journal as a venue for your work.

FDMP Editorial

Fluid Dynamics & Materials Processing

Tech Science Press

ISSN: 1555-256X (print)

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871 Coronado Center Drive, Suite 200

Henderson, Nevada, 89052, USA

[fdmp] Editor Decision

noreply@tspsubmission.com <noreply@tspsubmission.com>

on behalf of

Jane Wang <vitawong75@hotmail.com>

Mon 22/06/2020 15:24

To: Sulardjaka <sulardjaka@lecturer.undip.ac.id>; Sri Nugroho <srinugroho2004@yahoo.com>; Norman Iskandar <norman.undip@gmail.com>; Agus Purnomo Adi <adiaguspurnomoadi@yahoo.com>; Deni Fajar Fitriyana <deniifa89@gmail.com>

Sulardjaka Sulardjaka, Sri Nugroho, Norman Iskandar, Agus Purnomo Adi, Deni Fajar Fitriyana:

We have reached a decision regarding your submission to Fluid Dynamics & Materials Processing, "Zeolite A Prepared from Geothermal Waste by Microwave-Hydrothermal and Conventional-Hydrothermal".

Our decision is: Revisions Required

Fluid Dynamics & Materials Processing  
Tech Science Press  
Henderson, Nevada, 89052, USA

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Reviewer A:

**Decision: Reject publication in current form – major revision required.**

The paper describes the preparation of zeolite from geothermal waste. This topic has been studied before and is generally worthy of publication but the paper in its current form is not of a sufficient standard to be published and will require a major revision to be considered for review. The major points are as follows:

1. The quality of English needs to be significantly improved throughout the manuscript. The most common examples are misuse of articles; numerous spelling mistakes e.g. calcinated instead of calcined; incorrect grammar; and inconsistent styles e.g. natrium silicate and sodium silicate, grs and grams..... The manuscript will require changes to all these issues throughout.
2. This is not the first example of geothermal waste to zeolite. This fact does not negate the possibility of publishing the results in the manuscript and the authors have rightly included a reference to their own work *Sulardjaka, S.Nugroho, D.F. Fitriyana. (2014). Synthesis of zeolite from geothermal waste, Applied Mechanics and Materials, Vol. 660, 157-161. However, for a fuller literature review there is a more recent paper that should be included in any revised edition, see Methane oxidation over zeolite catalysts prepared from geothermal fluids, Microporous Mesoporous Mater. 285 (2019) 56-60.*
3. XRD results Figure 1 – the authors claim the presence of zeolite A in the sample after 20 mins but the peaks differ from those after 40 mins and 60 mins. Why, for example, are there no zeolite A peaks below 10° after 20 mins?
4. SEM – Figure 8 (c) and (e) are the same as (d) and (f). The discussion of the SEM results needs to be improved, at present it contains assertions without any clear reasoning.
5. Reference 24?

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Reviewer B:

**Review of "Zeolite A Prepared from Geothermal Waste by Microwave-Hydrothermal and Conventional-Hydrothermal"**

The authors proposed the use of geothermal waste as a silica resource and successfully synthesized Zeolite A by microwave-hydrothermal and conventional-hydrothermal. The effect of aging time and holding time on microwave hydrothermal on synthesized products have been studied. This work is interesting. But there are still some problems as follows.

- (1) References or standard spectrum should be cited for the phase attribution of XRD.
- (2) There are still some misspellings errors in this manuscript, e.g. "SiO2" in the first sentence of the third part. Please check the manuscript more carefully.
- (3) Symbols in equation 1 need to be rearranged.
- (4) The attribution of characteristic peaks in infrared spectrum needs to be cited.

Considering the standards of the journal, the article needs to make the above modifications. Therefore, I recommended major modification.

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Reviewer N:

The manuscript by Sulardjaka et al. describes the use of geothermal waste for the synthesis of zeolite A. Conventional and microwave heating were employed for the hydrothermal treatment, which was performed after two aging times of the precursor solution. No pure zeolite phases were reported and since control experiments using conventional zeolite precursors are missing, it is not clear whether the reason is the use of geothermal waste or poor design of the experiments. The geothermal waste used is not well-characterised, and the conditions of the pre-calcination procedure are not justified. XRD of the geothermal is not shown. The XRD patterns presented are not correctly discussed and most of the XRD patterns shown in Figures 1-3 do not actually correspond to zeolite A.

-----  
Reviewer Y:

The considered issues is essentially related to zeolite prepared from geothermal waste, which brings out the interests for the relevant designers and reseraches, nothing related to the innovation of the considered issue used for the comparison is used, please following the review comments below,

- 1) The literature related to the materials analysis and data's distribution is not well illustrated. Especially model structural design, proceed architecture, as well as the authors' references to be analyzed in the real issue, should be considered in detail.
- 2) Please provide the basic verification for the results that repoted in table 1 Chemical composition of geothermal powder.
- 3) Tabulate the results that reported in the tables 1-3 for comparison, especially, the performance indicator that can be used to verify the system description in the idea situation.
- 4) More detailed information should be considered in the processing architecture, such as the eliminated condition for the process of synthetic zeolite 2 h ageing of SEM image.
- 5) The result of the experiment that reported in Figs. 8-9 are not quantified and compared with the similar engineering issues also.
- 6) Please keep the literature of this paper updated.

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**Revision Guidelines from FDMP editorial office:**

1. Reference to specific geographical places (countries, cities, and locations), specific universities and laboratories should be avoided at all costs. Similarly, text such as "in our laboratory", "National industry", "domestic industry", "foreign industry", "foreign products" or "foreign market" should not be used.
2. If the paper is based on numerical simulations, the author must include the following distinct sections: Mathematical model, numerical method, validation and grid refinement study (with the "mesh sensitivity analysis" table).
3. Please check the language, grammar, syntax carefully and make sure the paper is readable and free of grammatical mistakes.
4. While submitting the revision, please make the followings both included:
  - 1) Please upload a modified version;
  - 2) Please upload a cover letter;In the cover letter, you need outline every change made point by point, and provide a suitable response for any comment provided by the Reviewer (comment-by-comment). **It's better to use different color to mark your responses.**

**Basic format of cover letter:**

Comment 1: \*\*\*\*  
Response: \*\*\*\*

Comment 2: \*\*\*\*  
Response: \*\*\*\*

...  
Please upload the above 2 mentioned files via your FDMP submission dashboard and please leave us a message. Thank you very much!

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Reviewer A:

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1. Comment:

The quality of English needs to be significantly improved throughout the manuscript. The most common examples are misuse of articles; numerous spelling mistakes e.g. calcinated instead of calcined; incorrect grammar; and inconsistent styles e.g. natrium silicate and sodium silicate, grs and grams..... The manuscript will require changes to all these issues throughout.

Response:

Thank you very much for your suggestion. We have improved the English language. The English language have been improved, some spelling mistakes and incorrect grammar have been corrected. (write by red ink)

2. Comment:

This is not the first example of geothermal waste to zeolite. This fact does not negate the possibility of publishing the results in the manuscript and the authors have rightly included a reference to their own work *Sulardjaka, S.Nugroho, D.F. Fitriyana. (2014). Synthesis of zeolite from geothermal waste, Applied Mechanics and Materials ,Vol. 660, 157-161.* However, for a fuller literature review there is a more recent paper that should be included in any revised edition, see *Methane oxidation over zeolite catalysts prepared from geothermal fluids, Microporous Mesoporous Mater. 285 (2019) 56-60.*

Response:

Thank you very much for your suggestion. We had added 4 papers in the literature review, in referece 13, 14, 15 and 16 (write by red ink)

3. Comment:

XRD results Figure 1 – the authors claim the presence of zeolite A in the sample after 20 mins but the peaks differ from those after 40 mins and 60 mins. Why, for example, are there no zeolite A peaks below 10° after 20 mins? The authors will need to provide a much better explanation of the XRD results. The same applies for Figures 2 and 3.

Response:

Thank you very much for your question, there are zeolite A after 20 minute, but longer holding time, there are phase transformation ti produced sodalite.

4. Comment:

SEM – Figure 8 (c) and (e) are the same as (d) and (f). The discussion of the SEM results needs to be improved, at present it contains assertions without any clear reasoning.

Response:

Thank you very much for your suggestion. We agree with the reiewer that Figure 8 (c) and (e) are the same as (d) and (f). We have changed figure 8(e) and 8(f).

5. Comment:

Reference 24?

Response:

Thank you very much for your suggestion. Reference 24 corrected, it deleted from manuscript.

Reviewer B:

**Review of "Zeolite A Prepared from Geothermal Waste by Microwave-Hydrothermal and Conventional-Hydrothermal"**

The authors proposed the use of geothermal waste as a silica resource and successfully synthesized Zeolite A by microwave-hydrothermal and conventional-hydrothermal. The effect of aging time and holding time on microwave hydrothermal on synthesized products have been studied. This work is interesting. But there are still some problems as follows.

1. Comment:

References or standard spectrum should be cited for the phase attribution of XRD.

Response:

Thank you very much for your suggestion. We add standart spectrum for zeolite A and sodalite. Write in red ink and yellow background.

2. Comment:

There are still some misspellings errors in this manuscript, e.g. "SiO<sub>2</sub>" in the first sentence of the third part. Please check the manuscript more carefully.

Response:

Thank you very much for your suggestion. Some misspellings errors have been corrected by colored ink.

3. Comment:

Symbols in equation 1 need to be rearranged.

Response:

Thank you very much for your suggestion. Symbols in equation 1 had been rearranged (write with yellow background)

4. Comment:

The attribution of characteristic peaks in infrared spectrum needs to be cited.

Response:

Thank you very much for your suggestion. We add standart for analysed FTIR results. Write in red ink and yellow background.

Reviewer N:

Comment:

The manuscript by Sulardjaka et al. describes the use of geothermal waste for the synthesis of zeolite A. Conventional and microwave heating were employed for the hydrothermal treatment, which was performed after two aging times of the precursor solution. No pure zeolite phases were reported and since control experiments using conventional zeolite precursors are missing, it is not clear whether the reason is the use of geothermal waste or poor design of the experiments. The geothermal waste used is not well-characterised, and the conditions of the pre-calcination procedure are not justified. XRD of the geothermal is not shown. The XRD patterns presented are not correctly discussed and most of the XRD patterns shown in Figures 1-3 do not actually correspond to zeolite A.

Response:

Thank you very much for your corrections and suggestions. Focus of this paper was to produce zeolite A, but we conducted the experiment in variation of: hydrothermal process with 3, 4, 5 holding time (2 h ageing time) and variation of ageing time (2, 5 h) in microwave hydrothermal (20, 40, 60 minutes). From this variable process produced zeolite A and sodalite. At holding time 20 minute (2 h ageing time) and at holding time 20 and 40 minute (5 h ageing time) higher zeolite A was produced. At longer holding time zeolite A transformed into sodalite.

The geothermal waste used is not well-characterised, and the conditions of the pre-calcination procedure are not justified because we have reported that in our previous article (ref. 12 and ref. 27)



Reviewer Y:

The considered issues is essentially related to zeolite prepared from geothermal waste, which brings out the interests for the relevant designers and reseraches, nothing related to the innovation of the considered issue used for the comparison is used, please following the review comments below,

1. Comment:

The literature related to the materials analysis and data's distribution is not well illustrated. Especially model structural design, proceed architecture, as well as the authors' references to be analyzed in the real issue, should be considered in detail.

Response:

Thank you very much for your suggestions. The references have been analized more detail.

2. Comment:

Please provide the basic verification for the results that repoted in table 1 Chemical composition of geothermal powder.

Response:

The results of chemichal composition of geothermal powder was compared by results from Munfarida et.al (2020).

3. Comment:

Tabulate the results that reported in the tables 1-3 for comparison, especially, the performance indicator that can be used to verify the system description in the idea situation.

Response:

Thank you very much for your suggestions.

4. Comment:

More detailed information should be considered in the processing architecture, such as the eliminated condition for the process of synthetic zeolite 2 h ageing of SEM image.

Response:

Thank you very much for your suggestion. Information for 2 h ageing of SEM image has been added.

5. Comment:

The result of the experiment that reported in Figs. 8-9 are not quantified and compared with the similar engineering issues also.

Response:

Thank you very much for your suggestion. Figure 8-9 have been corrected.

6. Comment:

Please keep the literature of this paper updated.

Response:

Thank you very much for your suggestion. The literatures of this paper updated have been updated, we added 4 new literatures (literature 13, 14, 15 and 16) in literature review.

# Zeolite A Prepared from Geothermal Waste by Microwave-Hydrothermal and Conventional-Hydrothermal

Sulardjaka Sulardjaka<sup>1,\*</sup>, Sri Nugroho<sup>1</sup>, Norman Iskandar<sup>1</sup>, Agus P. Adi<sup>1</sup>, Deni F. Fitriyana<sup>2</sup>

<sup>1</sup>Diponegoro University, Jl. Prof. Sudarto, Semarang, 50275, Indonesia

<sup>2</sup>State University of Semarang, Gunungpati, Semarang, 50229, Indonesia

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Received: XXXX; Accepted: XXXX

**Abstract:** Zeolite A was successfully synthesized from geothermal waste by microwave-hydrothermal and conventional-hydrothermal. Geothermal waste was used as an alternative silica source for the synthesis of zeolite A. The reaction of geothermal waste with sodium aluminate and sodium silicate under microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) reaction led to the successful transformation of zeolite A. The microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) were done with the variation of ageing and synthesis time. The products were characterized using X-Ray Diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). In M-H process, zeolite formed at relatively low temperature (100 oC) in a short holding time (40 min). The crystallization of zeolite A was promoted with an increase of ageing and synthesis time. It was found that using M-H method, zeolite A was formed in shorter holding time. Zeolite A that was produced by M-H process has a smaller and more homogeneous crystal size than C-H method.

**Keywords:** Geothermal waste, microwave-hydrothermal, conventional-hydrothermal, zeolite A

## 1 Introduction

Indonesia is once of the country that has a high potential for geothermal energy. Indonesia has about 28 GW potential of geothermal energy and electricity production based on geothermal sources. In the production of geothermal energy, geothermal power plants produce geothermal waste (geothermal sludge and geothermal brine) in large quantities. The geothermal waste is a byproduct from geothermal power plants, in which the water and steam extracted from the underground are used to generate electricity [1,2].

Zeolites are crystals consisting of aluminate and silicate frameworks. Zeolites have the ability to act as catalysts, adsorbents and so on. As a consequence of their properties, zeolites have many potential applications in the fields of petrochemical reactions, water purification, and the purification of gasses [3-5]. Zeolite A is one of kind of zeolites. Due to its large ion exchange capacity, mechanical strength and particular crystal shape, zeolite A used to substitute sodium tripolyphosphate in the area of detergent and water softening.

In the synthesis of zeolite A, sodium silicate and sodium aluminate are the most commonly used Si and Al resources. One of problem on zeolite synthesis is the availability and cost of raw material specifically the silica source. In order for reducing the production cost of synthesized zeolite, many researchers have been purposed alternative materials as silica source. Some natural minerals and wastes, such as natural clinoptilolite, oil shale ash, municipal solid waste ash, rice husk ash and coal fly ash were used to replace sodium silicate in the synthesis of zeolite A for the cost-saving and environmental protection purposes [6-11]. Geothermal waste has high potential to be used as an alternative silica source for the synthesis of zeolite



A due to its silica contents. In our previous study, by a conventional-hydrothermal process, geothermal waste has successfully converted into zeolite A and sodalite [12]. Colloidal silica extracted from geothermal fluid was successfully synthesized to produced low Si/Al zeolite Y with similarity characteristics compared to zelite Y prepared from a conventional silica sol, Ludox [13]. Hydrothermal at temperature 150 °C for 5 hours with concetration of NaOH 3 M produced Zeolite X with octahedral crystal shape and having a specific surface area of 68.985 m<sup>2</sup>/gr and a pore volume of 0.109 cc/gr. The zeolite synthesized from this geothermal waste and processes was successfully used as a catalyst for enhanced biohydrogen production [14, 15]. Colloidal silica extracted from geothermal fluids can be used as silica source for zeolite synthesis [16]. The purity and yield of zeolite A synthesized from natural minerals and wastes using hydrothermal treatment were limited to the SiO<sub>2</sub> extraction from them. In order to increase the yield of SiO<sub>2</sub> and synthetic zeolite, several methods, such as: calcining, alkali and acid activation were conducted to treat these raw materials before the synthesis process of zeolite [12,17].

Several synthesis methods have been purposed for increasing yield and purity of zeolite synthesis. Besides conventional hydrothermal, some authors have been purposed synthesis zeolite by microwave hydrothermal. Numerous papers on the subject of microwave-hydrothermal (M-H) synthesis of zeolites have been published [9,18,19]. These papers concluded that application of microwaves on the zeolite synthesis, give the significant reduction in crystallization time due to faster and homogeneous heating compared to conventional-hydrothermal (C-H). However, the fast temperature rise induced in the reacting solution by microwaves affects the nuclei formation leading to the crystallization of undesired phases or, sometimes, to the precipitation of amorphous solids [20,21]. Ageing the solution or adding seeds were proved to bring a beneficial effect to nucleation in microwave synthesis of various zeolites [22]. Chu et al. (1998) were the first to show that microwave heating could be used for the rapid synthesis of zeolites, crystallization of zeolite NaA was obtained in 12 min but the product was contaminated with hydroxysodalite (HS), even if the mixture was aged for 2 h at room temperature before microwave heating [22]. Slangen et.al.(1997) were able to obtain pure zeolite A in 5 min crystallization, but after 20 h of ageing at room temperature. Whereas, zeolite A with little hydroxysodalite could be obtained in as little as 4 h of ageing [23]. In a laboratory scale, the microwave zeolite synthesis usually consists in a batch reaction run in an autoclave made of a material transparent to microwaves, irradiated at 2.45 GHz in a multimodal oven cavity, like the customary household microwave ovens [19, 25].

This study used geothermal waste as silica sources to produce synthesized zeolite A. Zeolite A was synthesized from the calcined geothermal waste. The calcined geothermal waste was added into alkali solution and aluminium source and followed by microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) method. The effects of ageing and crystallization time, on the formation of zeolite A, were also investigated.

## 2 Materials and Methods

Geothermal sludge was obtained from Geo Dipa Energy Co. Ltd. (Wonosobo, Central Java, Indonesia). Then, geothermal waste was dried under the sunlight and sievec with a 320 mesh of sieving machine. This process resulted as receive geothermal powder. The powder was calcined by burned at temperature 850 °C for 3 hours at atmospheric condition using Carbolite furnace. Calcining process was carried out to burn unexpected or volatile materials. The chemical compositions of geothermal waste before and after calcining were characterized by atomic absorption spectroscopy (AAS) using Shimadzu type AA-6650 and the results presented in the form of stable oxides as shown in Tab. 1.

The first step for zeolite synthesis is making sodium silicate. In this research, sodium silicate was made from 3 gr of geothermal waste mixed with 30 mL of NaOH 5 M. This mixtures were stirred at a temperature of 100 °C for 20 min. Sodium aluminate was made from 20 g of NaOH 5 M dissolved in distilled water to yield 100 ml of 5 M NaOH and then added 9 gr of Al(OH)<sub>3</sub> gradually while stirring at a temperature of 100 °C for 20 min. The two suspensions: 30 mL of sodium silicate and 30 mL of sodium aluminate were mixed and stirred using a magnetic stirrer with 200 rpm for 2 and 5 hours ageing time at room temperature. The moment the silica was added was taken as the beginning of ageing. The ageing time thus includes the

dissolution of silica into alumina solution [22]. From this step resulted precursor gel for zeolite A synthesis.

**Table 1:** Chemical composition of geothermal powder

Compound	Before <b>Calcining</b> (wt. %)	After <b>Calcining</b> (wt,%)
Al <sub>2</sub> O <sub>3</sub>	0.055	0.142
Fe <sub>2</sub> O <sub>3</sub>	0.192	0.451
Na <sub>2</sub> O <sub>3</sub>	0.609	0.760
SiO <sub>2</sub>	49.100	80.043

A household-type microwave oven 2.45 GHz (Panasonic NN-SM320M) with maximum output power 450 Watt was used for the microwave synthesis. For measuring the temperature of the process, the thermocouple was inserted into the microwave. The precursor gel was poured into a Teflon(R) box and placed into the microwave and heated at 100°C for 20, 40 and 60 min. Teflon(R) autoclave with controllable heating was used for conventional hydrothermal process. Conventional hydrothermal was done by pouring the precursor gel into the Teflon(R) autoclave and heated until 100 °C with holding time 3, 4 and 5 hours. Synthesized products were washed with aquabidest and filtered with whatmann 42 paper to separate between solid and filtrate. The solid powder was dried in the oven at a temperature of 80 °C for 4 hours. The powders were analyzed by Rigaku X-ray diffractometer using CuK $\alpha$  radiation (40 kV, 30 mA), 8201PC Shimadzu FTIR (Fourier Transform Infra-Red) and JEOL JSM 6300 SEM (Scanning Electron Microscope).

### 3 Results and Discusions

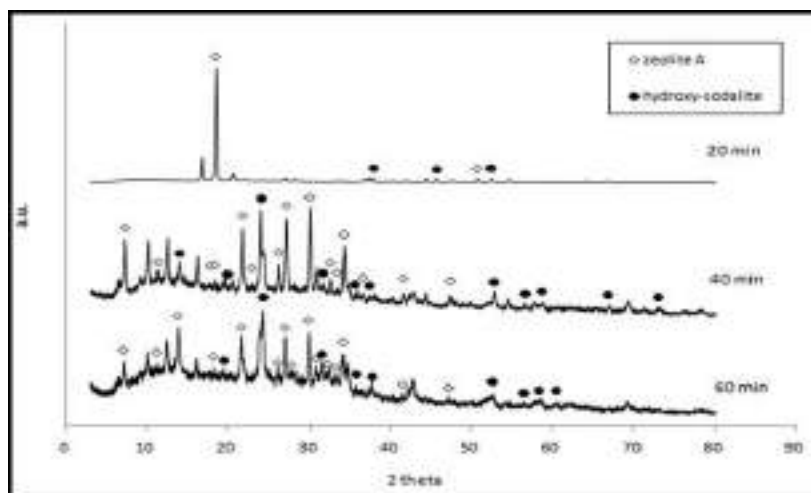
Tab. 1 shows that the geothermal powder before **calcining** contains 49.10% SiO<sub>2</sub>, and after **calcining**, the amount of SiO<sub>2</sub> increase up to 80.04 %. **Calcining** process causes unexpected and volatile materials were burned out. **Calcined** geothermal wasted produced Si/Al ratio 1.79 as shown on Table 2. The ratio of Si/Al allows the formation of zeolite A, which according to the literature that zeolite A has a ratio of Si/Al with range 1-3.5 [21]. Sulardjaka et.al (2014) has reported that the geothermal powder before **calcining** contains silica in amorphous form, there is no dominant peak from the diffractogram. However, the peaks are found at 21.91 and 20.88 in the **calcined** geothermal powder. It indicates that there are transformation of amorphous silica into primary cristobalite [12]. The **calcining** process until 850 °C for 3 hours, some of the silica transforms **into** cristobalite phase, but the amorphous silica phase is still dominant phase [26,27]. SiO<sub>2</sub> in amorphous form in geothermal waste is potential as a silica resources for zeolite synthesis.

**Table 2:** Si/Al ratio of synthetic mixture

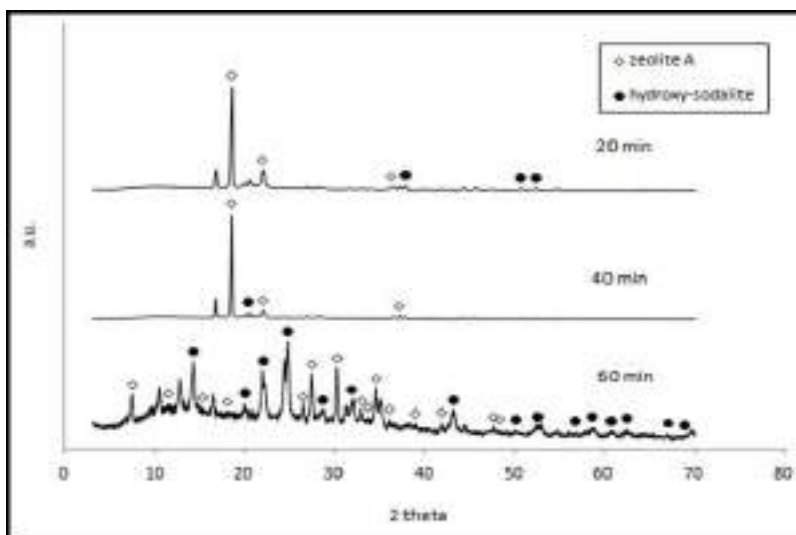
Sample	Element	Average (wt. %)
Precursor gel	Al	5.86
	Si	10.48

XRD diffraction pattern of synthesized products from microwave-hydrothermal of geothermal waste for 2 h and 5 h ageing time shown at Fig. 1 and Fig. 2 respectively. Phases produced from conventional-hydrothermal is shown in Fig. 3. **Based on the diffractogram pattern as shown in Fig. 1, Fig. 2 and Fig. 3, they has accordance with diffractogram from JCPDS data number 11-0401 (hydroxy-sodalite) and 31-1269 (zeolite A). It shows that the synthetic zeolite in all of variation contains crystal of zeolite A and sodalite.** Microwave-hydrothermal for 2 h ageing time, holding time for 20 minutes, phase zeolite A is dominant phase, increasing holding time to 40 and 60 minutes, phase zeolite A also increases and sodalite phase is formed. X-Ray diffraction of microwave-hydrothermal of geothermal waste for 5 h ageing with 20, 40 and

60 minutes show that at ageing for 20 and 40 minutes, zeolite A phase is dominant. The rise of holding time to 60 minutes, increases phase of zeolite A and produces sodalite phase.



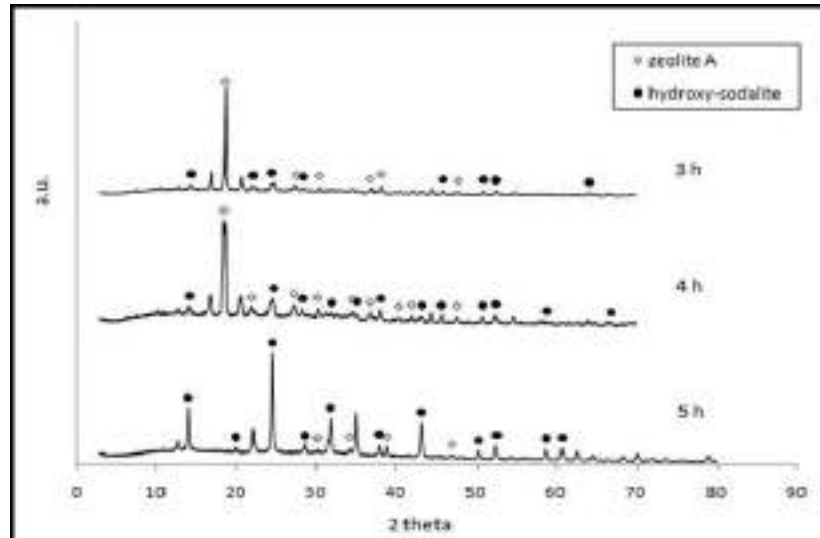
**Figure 1:** X-Ray diffraction of microwave-hydrothermal of geothermal waste for 2 h ageing with the variation of holding time



**Figure 2:** X-Ray diffraction of microwave-hydrothermal of geothermal waste for 5 h ageing with the variation of holding time

Fig. 3 shows X-Ray diffraction of conventional-hydrothermal of geothermal waste for 2 h ageing with 3, 4, 5 hours holding time. At holding time for 3 hours, produced zeolite A and less sodalite phase. The rise of holding time, increase zeolite A and sodalite phases. Holding time for 5 hours hydroxy-sodalite phase is dominant. The microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) of geothermal waste produced synthetic zeolite. Zeolites A and sodalite were produced in all of the variation of microwave-hydrothermal process. Along with increasing M-H time, it increases the production of zeolite A and sodalite. However, along with increasing C-H time, it decreased the zeolite A phase and increased the phase of sodalite. In zeolite A synthesis, formation of building units and nucleation of zeolite using the building units occur, followed by crystal growth by adsorption of building units on the surface of zeolite nuclei and crystal. At the longer holding time, the impurity phase of zeolite A is formed. There has been a

transformation from zeolite A  $\rightarrow$  sodalite. The surface-to-core extension of crystallization, sodalite nanoplates were crystallized within the amorphous cores of zeolite A. At longer holding time, sodalite nanoplates increased in size and breaking the cubic shells of zeolite A in the process, leading to the phase transformation from zeolite A to sodalite [27-29].



**Figure 3.** X-Ray diffraction of conventional-hydrothermal of geothermal waste for 2 h ageing with variation of holding time

The average of crystal grain size of synthesized zeolites can determine from the results of XRD graphs, it could be calculated using Scherer formula [30, 31].

$$L = \frac{57.3 \times k \times \gamma}{\beta \times \cos \theta} \quad (1)$$

Where:

$L$  = crystal grain size (nm),

$k$  = oxide constant (0.94),

$\lambda$  = X-ray wavelength (1.5406 Å),

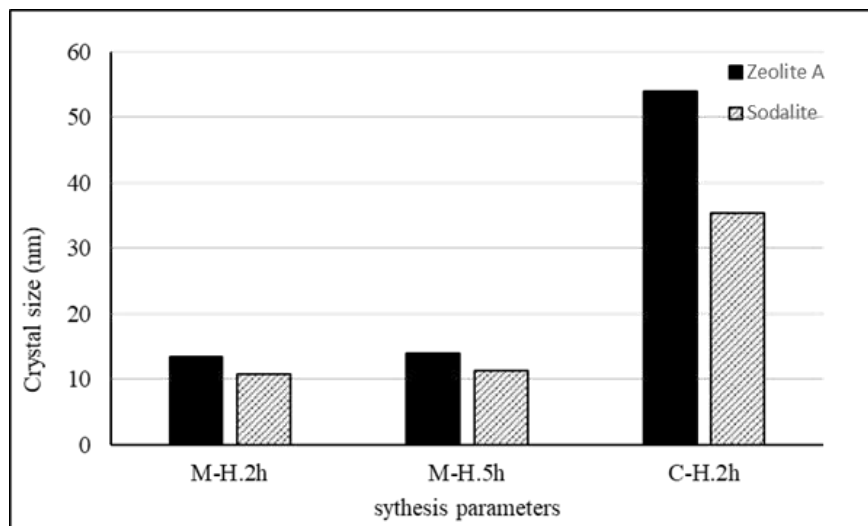
$\beta$  = the value of FWHM (deg),

$\theta$  = angle of crystal diffraction peak position (deg),

57.3 = correction factor from degree to radian.

The results of crystal grain size calculation using Scherer formula is shown in Figure 4. The crystal size of zeolite A produced from M-H are: 13.43 nm (ageing 2 h) and 14 nm (ageing 5 h). C-H with 2 h ageing produced zeolite A with crystal size 53.94 nm and sodalite with crystal size 35.4 nm. Sodalite with crystal size 10.78 nm (ageing 2 h) and 11.38 nm (ageing 5 h) were also formed from M-H. M-H produces smaller and more homogeneous crystal size of zeolite A and sodalite due to faster and homogeneous heating compared to conventional-hydrothermal (C-H). Ageing time with variation of 2 h and 5 h on M-H method affect nucleation and crystallization of synthetic zeolite. The ageing of precursor gels resulted in acceleration of the crystallization and crystal size diminution of the synthesis product, the ageing process directly influence to the concentration and number of formed nuclei [32]. Fast crystallization on M-H method affect the significant reduction of crystallization time, 3 or 4 times, shorter than C-H method. It was

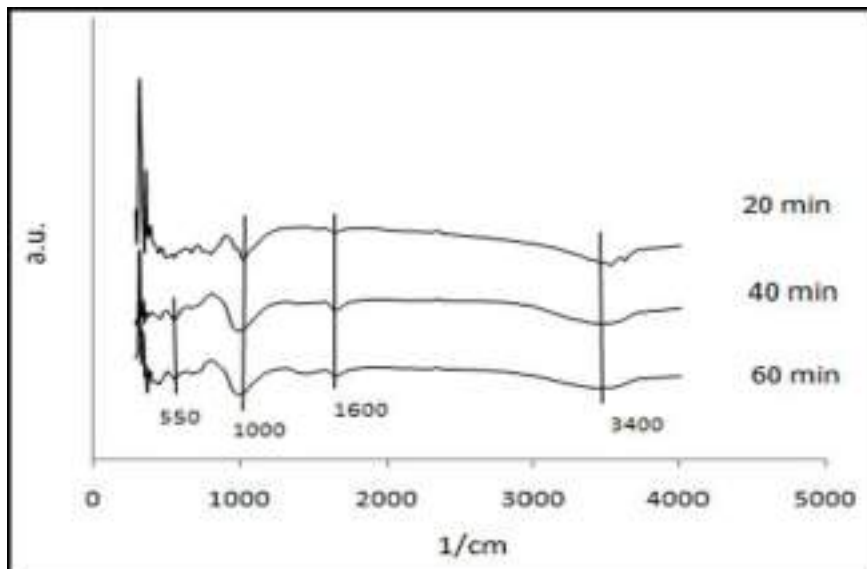
also observed that the time and temperature of microwave heating had significant effects on the prepared zeolite particles. The shortening of synthesis times in microwave heating is caused by two different mechanisms, i.e., the rapid heat-up of the sample and a better heat transfer which results in rapid and thorough heating of the synthesis mixture. This thorough heating can easily result in rapid and thorough heating of the synthesis mixture and effect on faster crystallization [33, 34].



**Figure 4:** Crystal size of zeolite A and hydroxy-sodalite

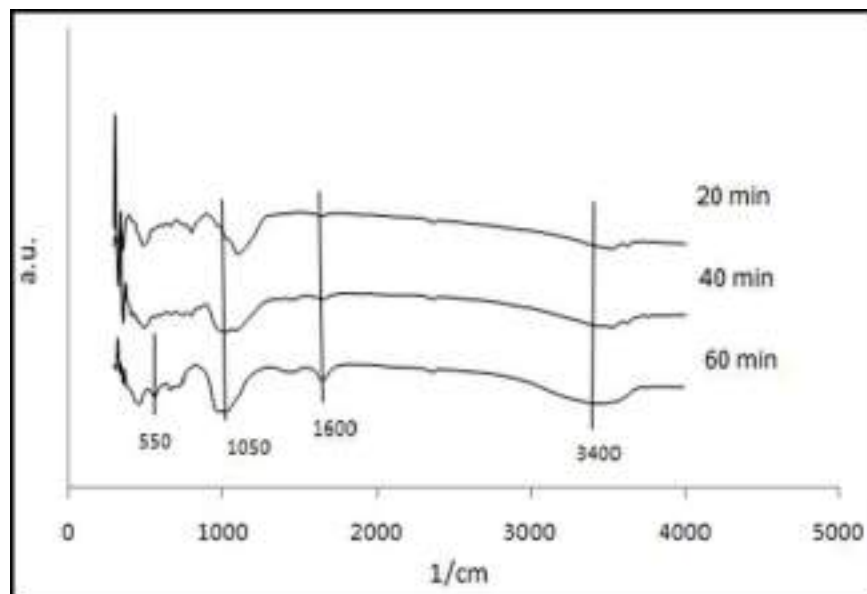
FTIR analysis was conducted to identify functional group on the synthetic zeolite. FTIR data were analysed based on The Nicodom FTIR Spectra Libraries. FTIR data were obtained from references such as the general FTIR vibrational region  $300-400\text{ cm}^{-1}$  (vibrations of the external opening of the pores caused by breathing motion of the ring hole 12), vibration region  $420-500\text{ cm}^{-1}$  (Si-O/Al-O bending vibrations) vibration region  $500-650\text{ cm}^{-1}$  (double ring D4R/ D6R external vibration) which shows the formation of zeolite A, vibration region  $650-850\text{ cm}^{-1}$  (symmetric stretching vibrations of O-Si-O or O-Al-O) vibration region  $900-1250\text{ cm}^{-1}$  (asymmetric stretching vibrations of O-Si-O or O-Al-O) vibration region  $1600-1700\text{ cm}^{-1}$  (O-H bending vibration) which showed the presence of zeolitic water ( $\text{H}_2\text{O}$ ) and vibration region  $3400-3700\text{ cm}^{-1}$  (O-H stretching vibration of Si-OH) [21]. FTIR spectra of zeolite synthesis results at 3 variations can be seen in Fig. 5, Fig. 6 and Fig. 7.



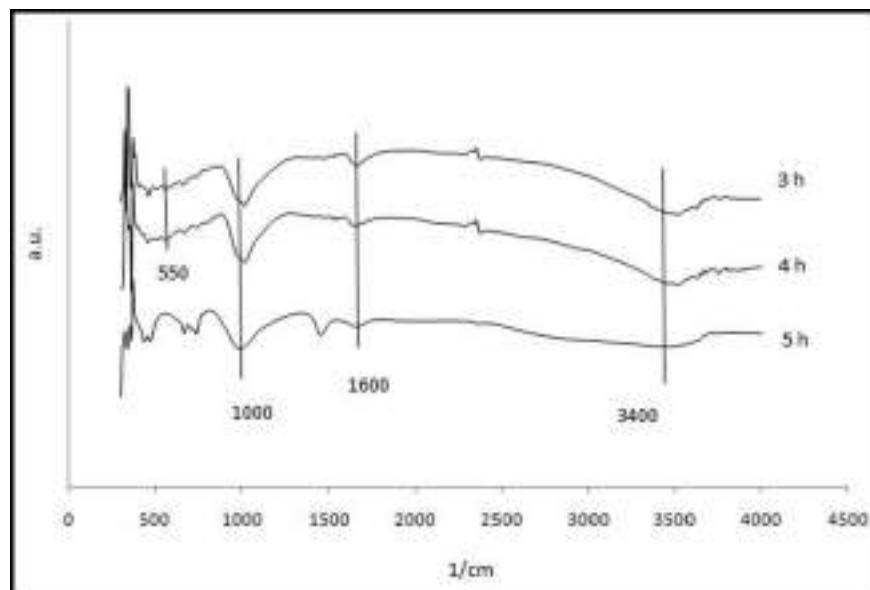


**Figure 5:** FTIR spectra of zeolite produced from microvawe-hydrothermal synthesis for 2 h ageing

There are wavenumber  $555.5\text{ cm}^{-1}$  and  $563.21\text{ cm}^{-1}$  for 40 and 60 min 2 h ageing; M-H. Existence of the absorption band in the region around  $500\text{-}650\text{ cm}^{-1}$  shows the double ring D4R or D6R. It can be concluded that zeolite A was only formed in variation 40 and 60 min 2 h ageing; M-H. There is only wavenumber  $563.21\text{ cm}^{-1}$  for 60 min 5 h ageing; M-H. It can be concluded that zeolite A was only formed in variation 60 min 5 h ageing; M-H. There are wavenumber  $555.5\text{ cm}^{-1}$  and  $555.5\text{ cm}^{-1}$  for 3 and 4 h, 2 h ageing; C-H. The FTIR analysis is match with the XRD analysis that zeolite A was only formed in variation 3 and 4 h, 2 h ageing; C-H.

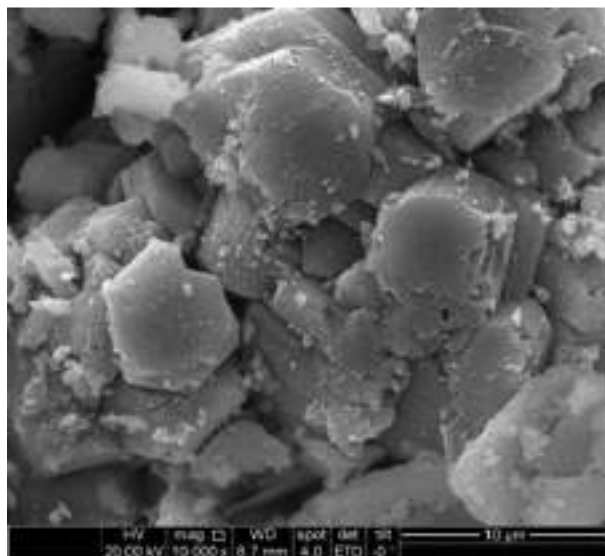


**Figure 6:** FTIR spectra of zeolite produced from microvawe-hydrothermal synthesis for 5 h ageing

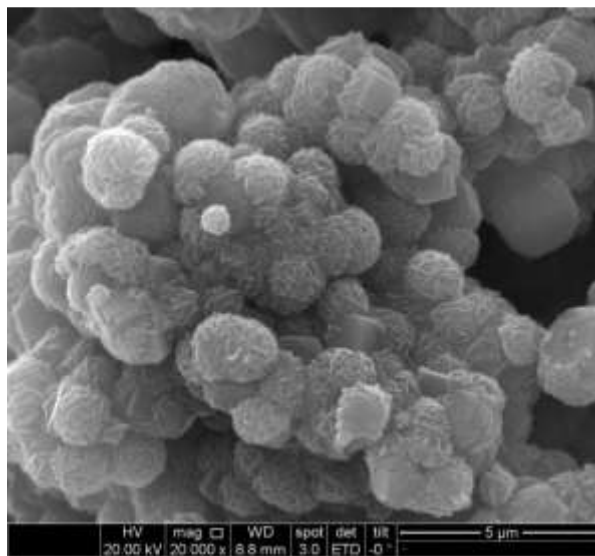


**Figure 7:** FTIR spectra of zeolite produced from conventional-hydrothermal synthesis for 2 h ageing

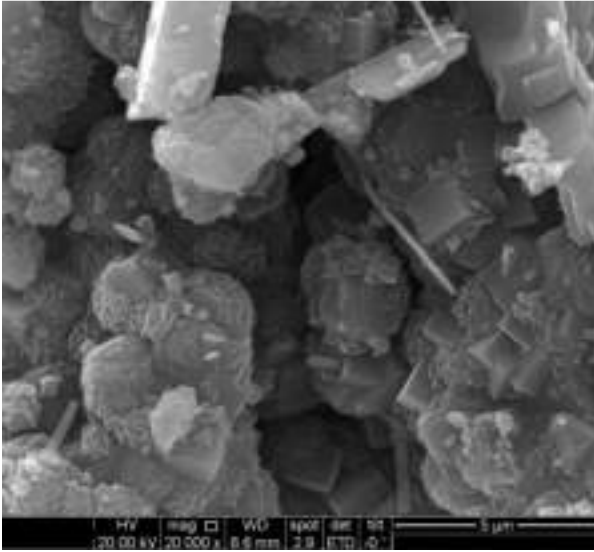
Scanning electron micrograph of the M-H process with 2 h ageing with holding time 20 min, 40 min and 60 min are shown in Fig. 8.a., 8.b. and 8.c respectively. It is shown that on variation 20 min, the form of grain is not regular or amorphous and zeolite A has not been formed yet. But, on variation 40 and 60 min, zeolite A and sodalite has been formed. Zeolite A has cubic form and sodalite has spherical form with an array of long fibers that surround it. Same with M-H with ageing 2 h, M-H with ageing time 5 h and holding time 20 min The zeolite A has not been formed, it is shown in Fig. 6.d. that the form of grain is not regular or amorphous. The spherical form appears on variation 40 min (Fig. 6.e). It reveals that amorphous silica transforms into a crystal of zeolite. On variation 60 min (Fig. 6.f.), the image shows the formation of many cubes which is a form of zeolite A and sodalite, which has the formation of spherical with an array of long fibres that surround it. The grain size of zeolite A and sodalite approximately 1  $\mu\text{m}$ .



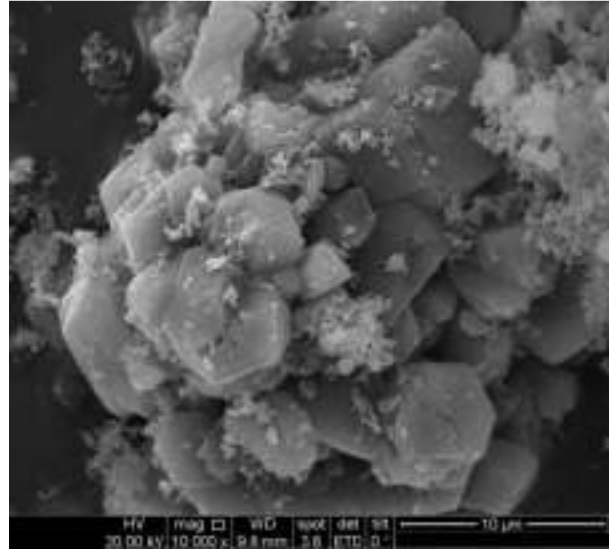
(a)



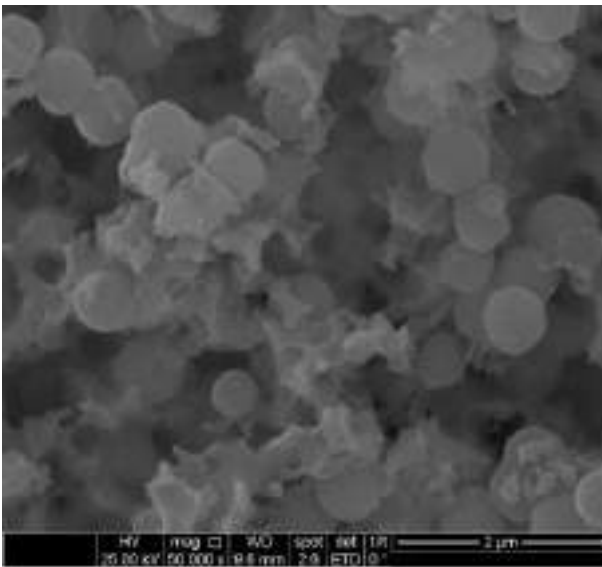
(b)



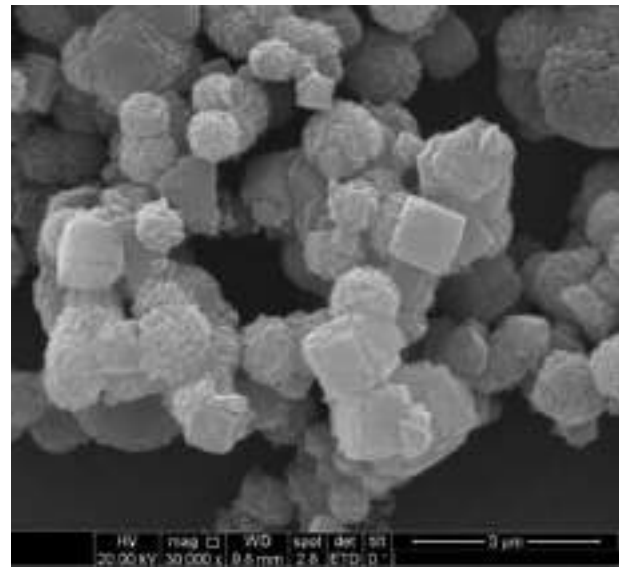
(c)



(d)



(e)

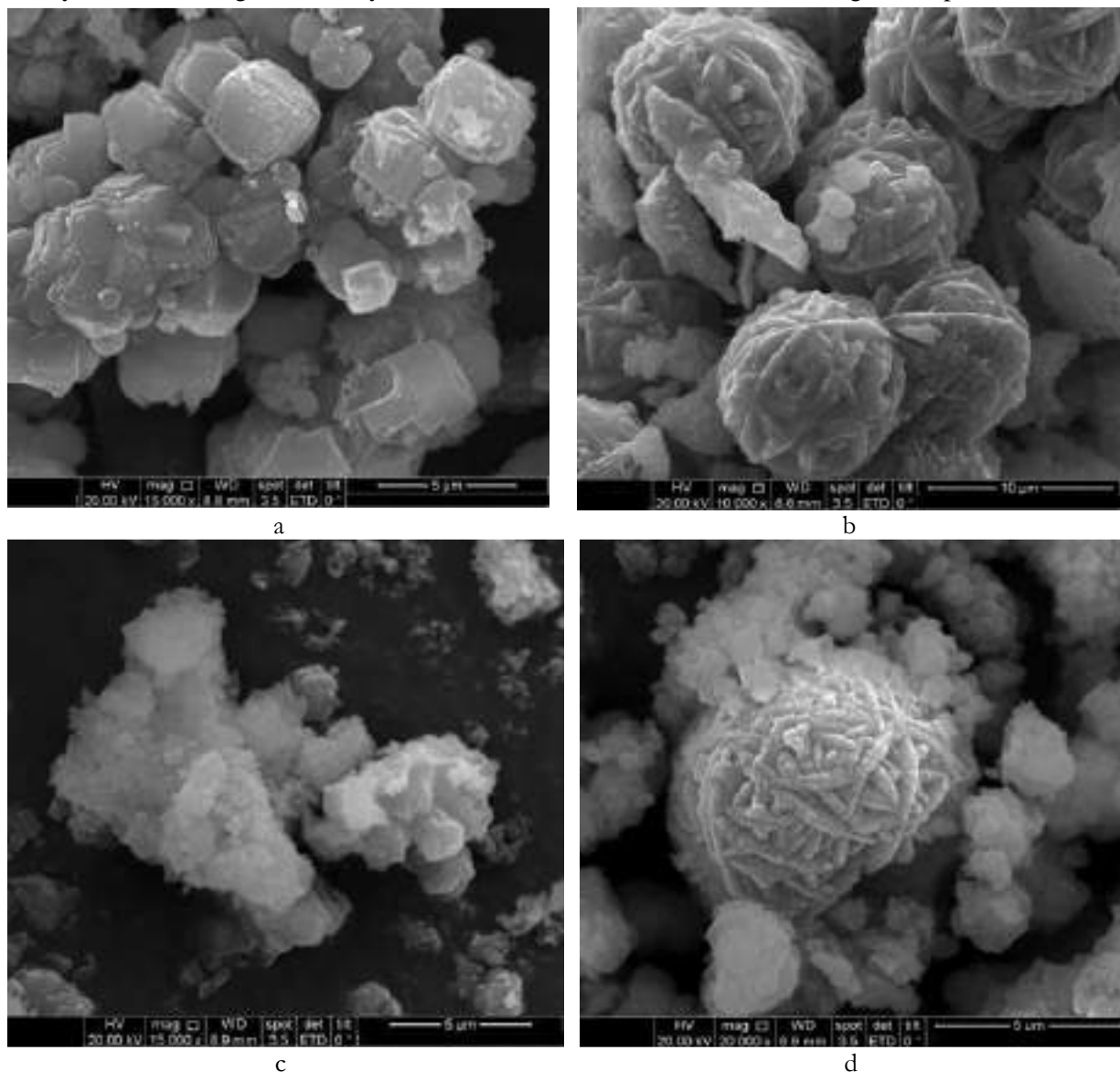


(f)

**Figure 8:** SEM image of synthetic zeolite for 2 h ageing; M-H (a) 20 min (b) 40 min (c) 60 min and 5 h ageing; M-H (d) 20 min (e) 40 min (f) 60 min

Result of the SEM on the variation 2 h ageing; C-H as shown in Fig. 9. On variation 3 h, It's shows the formation of zeolite A and sodalite with a grain size about 5  $\mu\text{m}$  and 10  $\mu\text{m}$  respectively (Fig. 9.a. and

Fig. 9.b.). Fig. 9.c. shows that formation of zeolite A and sodalite is not clear on variation 4 h, and only sodalite phase appears on variation 5 h because zeolite A has been transformed into sodalite (Fig 9.d.). M-H produces smaller and more homogeneous grain size of zeolite A and hydroxy-sodalite due to faster and homogeneous heating compared to conventional-hydrothermal (C-H). The formation of sodalite as a side product in the synthesis of NaA is not very surprising and can be explained by inadequate mixing. Prolonged heating then results in dissolution and regrowth of crystals of that composition, e.g., when a NaA mixture moves into a HS range, eventually, all NaA will be transformed into sodalite. However, when the synthesis mixture stays in the NaA region, the only sodaliteS that can nucleate is in the inhomogeneous pockets [32].



**Figure 9:** SEM image of synthetic zeolite 2 h ageing; C-H (a) 3 h; zeolite A (b) 3 h; sodalite (c) 4 h (d) 5 h

#### 4 Conclusions

Zeolite A was successfully synthesized from geothermal waste by conventional-hydrothermal (C-H) and microwave-hydrothermal (M-H). Geothermal waste consists of 80.04 %  $\text{SiO}_2$  and 0.142 %  $\text{Al}_2\text{O}_3$ , the silica content of geothermal waste is a high potential as an alternative silica source for synthesizing zeolite

A. The rise of M-H time will increase the crystallinity of zeolite A and sodalite but the rise of C-H time will decrease the crystallinity of zeolite A and increase the crystallinity of sodalite. Fast crystallization on M-H method affect the significant reduction of crystallization time 3 or 4 times shorter than C-H method and produces smaller and more homogeneous crystal size compared to C-H method.

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**Conflicts of Interest:** The authors declare that they have no conflicts of interest to report regarding the present study.

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Further process will be applied, you will be contacted shortly.

Thank you very much.

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Revise the Abstract as follows: Zeolite A has been successfully synthesized from geothermal waste with sodium aluminate and sodium silicate using conventional (C-H) and microwave heating (M-H) for the hydrothermal treatment. The products obtained for different aging times have been characterized using X-Ray Diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). It is shown that with the M-H process, zeolite can be formed at relatively low temperature (100 °C) in a relatively short time (40 min). The crystallization of zeolite A has been found to be generally promoted by an increase of aging and synthesis time; however, it has also been observed that relative long aging times can transform it into sodalite. Zeolite A produced through the M-H process generally displays a smaller and more homogeneous crystal size with respect to that obtained with the C-H method.

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## Zeolite A Synthesized from Geothermal Waste Using Conventional and Microwave Heating for the Hydrothermal Treatment

**Abstract:** Zeolite A has been successfully synthesized from geothermal waste with sodium aluminate and sodium silicate using conventional (C-H) and microwave heating (M-H) for the hydrothermal treatment. The products obtained for different aging times have been characterized using X-Ray Diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). It is shown that with the M-H process, zeolite can be formed at relatively low temperature (100 °C) in a relatively short time (40 min). The crystallization of zeolite A has been found to be generally promoted by an increase of aging and synthesis time; however, it has also been observed that relative long aging times can transform it into sodalite. Zeolite A produced through the M-H process generally displays a smaller and more homogeneous crystal size with respect to that obtained with the C-H method.

**Keywords:** Geothermal waste, microwave-hydrothermal, conventional-hydrothermal, zeolite A

### 1 Introduction

High potential of geothermal energy promising an alternative resource in power plant generation. In the production process, wastes are produced (geothermal sludge and brine) in large quantities, and are the byproducts from power plants, in which the water and steam extracted from the underground are used to generate electricity [1,2].

Zeolites are crystals consisting of aluminate and silicate frameworks, with the ability to act as catalysts, adsorbents, etc. As a consequence of their properties, they have many potential applications in the fields of petrochemical reactions, water and gas purification [3-5]. Zeolite A is a type of zeolites, and due to its large ion exchange capacity, mechanical strength, and particular crystal shape, it is used in the substitution of sodium tripolyphosphate in the aspect of detergent and water softening.

In the synthesis of zeolite A, sodium silicate and sodium aluminate are the most commonly used Si and Al resources. One of the problems in zeolite synthesis is the unavailability and cost of raw material, specifically the silica source. In order to reduce the production cost of synthesized zeolite, many alternative materials, such as silica source have been proposed. Some natural minerals and wastes, such as clinoptilolite, oil shale, municipal solid, rice husk and coal fly ash were used to replace sodium silicate in the synthesis of zeolite A for cost-saving and environmental protection purposes [6-11]. Geothermal waste has high potential to be used as an alternative silica source for the synthesis of zeolite A, due to its silica contents. In previous study, by a conventional-hydrothermal process, geothermal waste was successfully converted into zeolite A and sodalite [12]. Colloidal silica extracted from geothermal fluid was synthesized to low Si/Al zeolite Y, with similarity characteristics compared to those prepared from a conventional silica sol or Ludox [13]. Hydrothermal process at 150 °C for 5 hours with 3 M of NaOH produced Zeolite X with octahedral crystal shape, having a specific surface area of 68.985 m<sup>2</sup>/gr and a pore volume of 0.109 cc/gr. The synthesized zeolite was successfully used as a catalyst for enhancing biohydrogen production [14, 15]. The colloidal silica extracted from geothermal fluids is used as silica source for zeolite synthesis [16]. The purity and yield of zeolite A synthesized from natural minerals and wastes using hydrothermal treatment were limited to the SiO<sub>2</sub> extraction. In order to increase the yield of SiO<sub>2</sub> and synthetic zeolite, several



methods, such as calcining, alkali, and acid activation were conducted to treat these raw materials before the synthesis process [12,17].

Several synthesis methods have been proposed for increasing the yield and purity of zeolite, besides conventional hydrothermal, some synthetic zeolites by microwave hydrothermal were produced. Also, numerous studies on the subject of microwave-hydrothermal (M-H) synthesis of zeolites have been published [9,18,19]. This research explained that the application of microwaves on zeolite synthesis, yield significant reduction in crystallization time due to faster and homogeneous heating, compared to conventional-hydrothermal (C-H) method. However, the fast temperature rise induced in the reacting solution by microwaves affects the nuclei formation, leading to the crystallization of undesired phases, or to the precipitation of amorphous solids [20,21]. The addition of seeds or ageing the solution were proved to bring a beneficial effect to nucleation in microwave synthesis of various zeolites [22]. Chu et al. (1998) was the first to show that microwave heating is used for the rapid synthesis of zeolites, and the crystallization of zeolite NaA was obtained in 12 min, contaminated with hydroxysodalite (HS), even when the mixture was aged for 2 hrs at room temperature before the M-H treatment [22]. Slangen et.al.(1997) obtained pure zeolite A in 5 mins crystallization, and after 20 hrs of ageing at room temperature. While the product with little hydroxysodalite was obtained in as short as 4 hrs of ageing [23]. In a laboratory scale, the microwave zeolite synthesis usually consists a batch reaction carried out in an autoclave made of a material transparent to microwaves, irradiated at 2.45 GHz in a multimodal oven cavity, similar to the customary household type [19, 25].

This study used calcined geothermal waste as silica sources in synthesizing zeolite A. This waste was added into alkali solution and aluminum source, followed by microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) method. The ageing effects and crystallization time, on the formation of zeolite A were also investigated.

## 2 Materials and Methods

Geothermal waste from geothermal power plant was dried under the sunlight and sieved with a 320-mesh sieving machine. The powder was calcined by burning at 850 °C for 3 hours at atmospheric condition using Carbolite furnace. Calcining process was carried out to burn unexpected or volatile materials. The chemical compositions of geothermal waste before and after calcining were characterized by atomic absorption spectroscopy (AAS) using Shimadzu type AA-6650 and the results were presented in the form of stable oxides as shown in Tab. 1.

The first step for zeolite synthesis was making sodium silicate. In this research, sodium silicate was made from 3 gr of geothermal waste mixed with 30 mL of NaOH 5 M. These mixtures were stirred at 100 °C for 20 min. Then, sodium aluminate was made from 20 g of NaOH 5 M dissolved in distilled water to yield 100 ml of 5 M NaOH, and then added 9 gr of Al(OH)<sub>3</sub> gradually, while stirring at 100 °C for 20 min. The two suspensions: 30 mL of sodium silicate and 30 mL of sodium aluminate were mixed and stirred using a magnetic stirrer at 200 rpm for 2 and 5 hours ageing time at room temperature. The moment the silica was added, it was taken as the beginning of ageing. This included the dissolution of silica in alumina solution [22], from this step resulted precursor gel for zeolite A synthesis.

**Table 1:** Chemical composition of geothermal powder

Compound	Before Calcining (wt. %)	After Calcining (wt,%)
Al <sub>2</sub> O <sub>3</sub>	0.055	0.142
Fe <sub>2</sub> O <sub>3</sub>	0.192	0.451
Na <sub>2</sub> O <sub>3</sub>	0.609	0.760
SiO <sub>2</sub>	49.100	80.043

A household-type microwave oven 2.45 GHz (Panasonic NN-SM320M) with maximum output power 450 Watt was used for microwave synthesis. For measuring the temperature of the process, the thermocouple was inserted into the microwave. The precursor gel was poured into a Teflon(R) box and placed into the microwave and heated at 100°C for 20, 40, and 60 min. The Teflon(R) autoclave with controllable heating was used for conventional hydrothermal process. This was performed by pouring the precursor gel into the Teflon(R) autoclave and heated until 100 °C with holding time 3, 4, and 5 hours. The synthesized products were washed with aquabidest and filtered with whatmann 42 paper to separate between solid and filtrate. The solid powder was dried in the oven at 80 °C for 4 hours. The powders were analyzed by Rigaku X-ray diffractometer using CuK $\alpha$  radiation (40 kV, 30 mA), 8201PC Shimadzu FTIR (Fourier Transform Infra-Red) and JEOL JSM 6300 SEM (Scanning Electron Microscope).

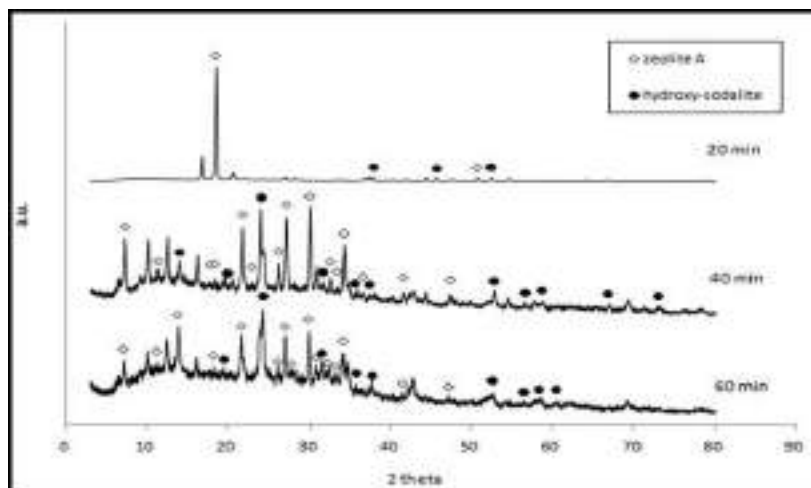
### 3 Results and Discussions

Tab. 1 shows that the geothermal powder before calcining contains 49.10% SiO<sub>2</sub>, and after, it increases up to 80.04 %. Munfarida et. al. has reported that using EDX analysis geothermal waste form power plant has SiO<sub>2</sub> containing 35.09 % and Al<sub>2</sub>O<sub>3</sub> about 0.05 % [26]. Calcining process causes unexpected and volatile materials to burned out. While the calcined geothermal waste produced Si/Al ratio 1.79 as shown on Table 2. This ratio allows the formation of zeolite A, which according to the literature that this product has a ratio of Si/Al ranging from 1-3.5 [21]. Sulardjaka et.al (2014) reported that the geothermal powder before calcining contained silica in amorphous form, there was no dominant peak from the diffractogram. However, the peaks were found at 21.91 and 20.88 in the calcined geothermal powder. This indicated that there was transformation of amorphous silica into primary cristobalite [12]. During the calcining process until 850 °C for 3 hours, some of the silica transformed into cristobalite phase, and the amorphous silica phase was still dominant [27,28]. SiO<sub>2</sub> in amorphous form in geothermal waste has potential as a silica resources for zeolite synthesis.

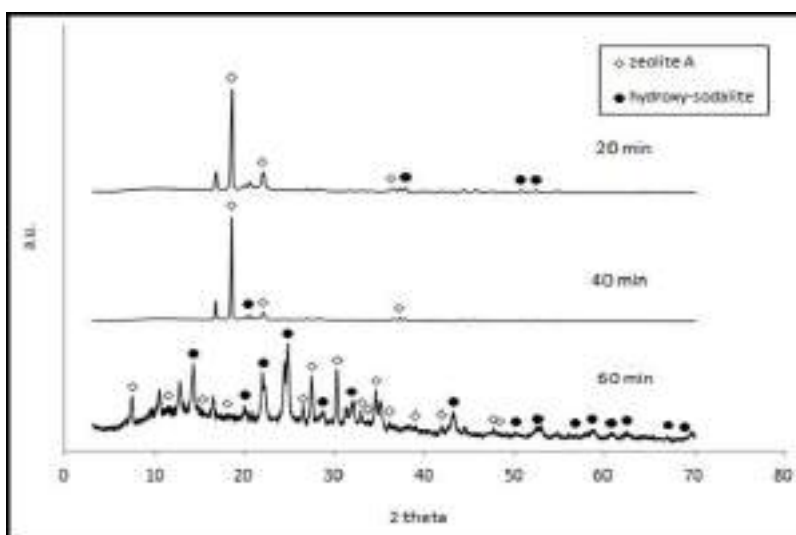
**Table 2:** Si/Al ratio of synthetic mixture

Sample	Element	Average (wt. %)
Precursor gel	Al	5.86
	Si	10.48

XRD diffraction pattern of synthesized products from microwave-hydrothermal of geothermal waste for 2 hrs and 5 hrs ageing time were shown at Fig. 1 and 2 respectively. The phases produced from conventional-hydrothermal were shown in Fig. 3. The diffractogram pattern as shown in Fig. 1, 2, and 3, correlated with that from JCPDS data number 11-0401 (hydroxy-sodalite) and 31-1269 (zeolite A). This showed that the synthetic zeolite in all the variation contained crystal of zeolite A and sodalite. During the microwave-hydrothermal for 2 h ageing, holding time for 20 mins, phase zeolite A became the dominant. While increasing the holding time to 40 and 60 mins, the zeolite A also increased and sodalite phase was formed. X-Ray diffraction of microwave-hydrothermal of geothermal waste for 5 hrs ageing showed that at the ageing of 20 and 40 mins, zeolite A phase was dominant. The rise of holding time to 60 mins, increased the zeolite A and produced sodalite phase.



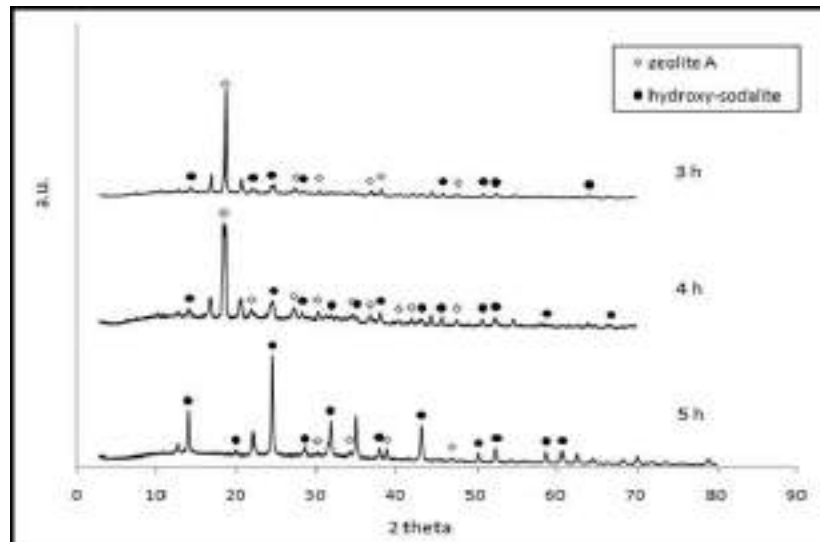
**Figure 1:** X-Ray diffraction of microwave-hydrothermal of geothermal waste for 2 hrs ageing with the variation of holding time



**Figure 2:** X-Ray diffraction of microwave-hydrothermal of geothermal waste for 5 hrs ageing with the variation of holding time

Fig. 3 showed X-Ray diffraction of conventional-hydrothermal of geothermal waste for 2 hrs ageing with 3, 4, 5 hours holding time. At the holding time of 3 hours, zeolite A and less sodalite phase were produced. The rise of holding time, increased zeolite A and sodalite phases. The holding time for 5 hours hydroxy-sodalite phase was dominant. The microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) of geothermal waste produced synthetic zeolite. Zeolites A and sodalite were produced in all of the variation of microwave-hydrothermal processes. The increasing M-H time, elevated the production of zeolite A and sodalite. However, the increasing C-H time, decreased the zeolite A phase and raised that of sodalite. In zeolite A synthesis, the formation of building units and the nucleation of zeolite with it, was followed by crystal growth by adsorption of the units on the surface of the zeolite nuclei and crystal. At the longer holding time, the impurity phase of zeolite A was formed. There has been a transformation from zeolite A  $\rightarrow$  sodalite. At the surface-to-core extension of crystallization, sodalite nanoplates were crystallized within the amorphous cores of zeolite A. At the longer holding time, sodalite nanoplates increased in size and breaking the cubic shells of zeolite A in the process. This led to the phase

transformation from zeolite A to sodalite [28-30].



**Figure 3.** X-Ray diffraction of conventional-hydrothermal of geothermal waste for 2 hrs ageing with variation of holding time

The average of crystal grain size of **synthesized** zeolites was determined from the results of XRD graphs, this was calculated using Scherer formula [31, 32].

$$L = \frac{57.3 \times k \times \gamma}{\beta \times \cos \theta} \quad (1)$$

Where:

L = crystal grain size (nm),

k = oxide constant (0.94),

$\lambda$  = X-ray wavelength (1.5406 Å),

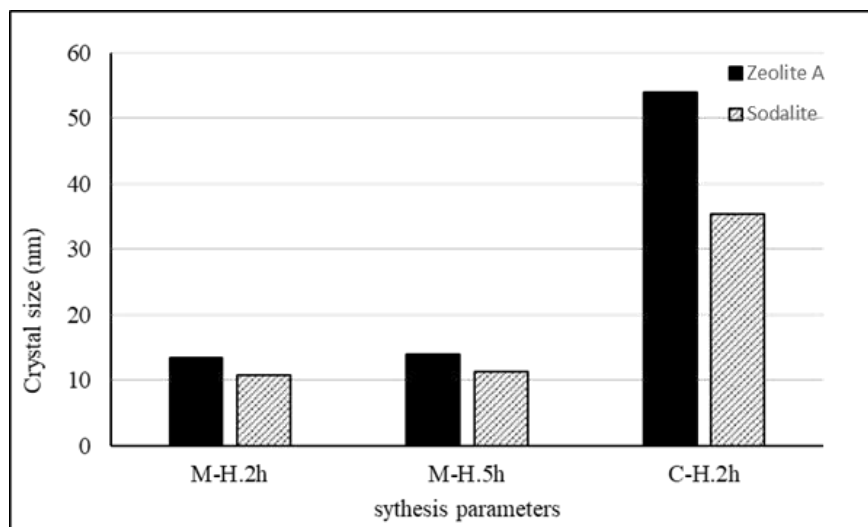
$\beta$  = the value of FWHM (deg),

$\theta$  = angle of crystal diffraction peak position (deg),

57.3 = correction factor from degree to radian.

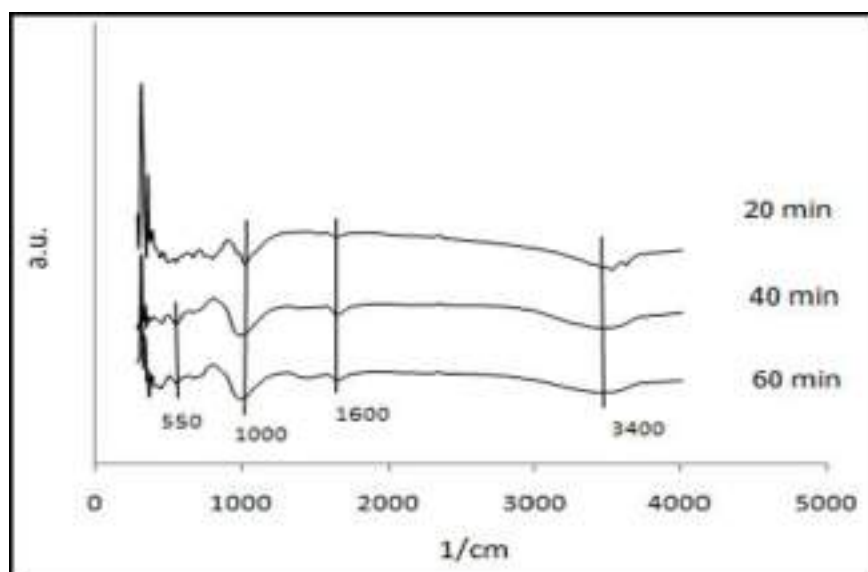
The results of the crystal grain size calculation using Scherer formula **was** shown in Figure 4. The crystal size of zeolite A produced from M-H **were** 13.43 nm (ageing 2 hrs) and 14 nm (ageing 5 hrs). **The** C-H with 2 hrs ageing produced zeolite A with crystal size of 53.94 nm, and sodalite of 35.4 nm. **The** sodalite with crystal size of 10.78 nm (ageing 2 hrs) and 11.38 nm (ageing 5 hrs) were also formed from M-H. **The** M-H produced smaller and more homogeneous crystal size of zeolite A and sodalite, due to faster and homogeneous heating compared to **the** C-H. Ageing time with variation of 2 and 5 hrs on **the** M-H method **affected** nucleation and crystallization of synthetic zeolite. The ageing of precursor gels resulted in the acceleration of the crystallization and crystal size diminution of the synthesis product. **This** ageing process directly **influenced** the concentration and number of formed nuclei [33]. The fast crystallization on M-H method **affected** the significant reduction of **its** time, 3 or 4 times, shorter than **that of** C-H method. It was also observed that the time and temperature of microwave heating had significant effects on the prepared zeolite particles. The shortening of synthesis times in microwave heating **was** caused by two different mechanisms, i.e., the rapid heat-up of the sample and a better heat transfer which **resulted in the**

rapid and thorough heating of the synthesis mixture. This easily resulted in rapid and vivid heating of the synthesis mixture and effect a faster crystallization [34, 35].



**Figure 4:** Crystal size of zeolite A and hydroxy-sodalite

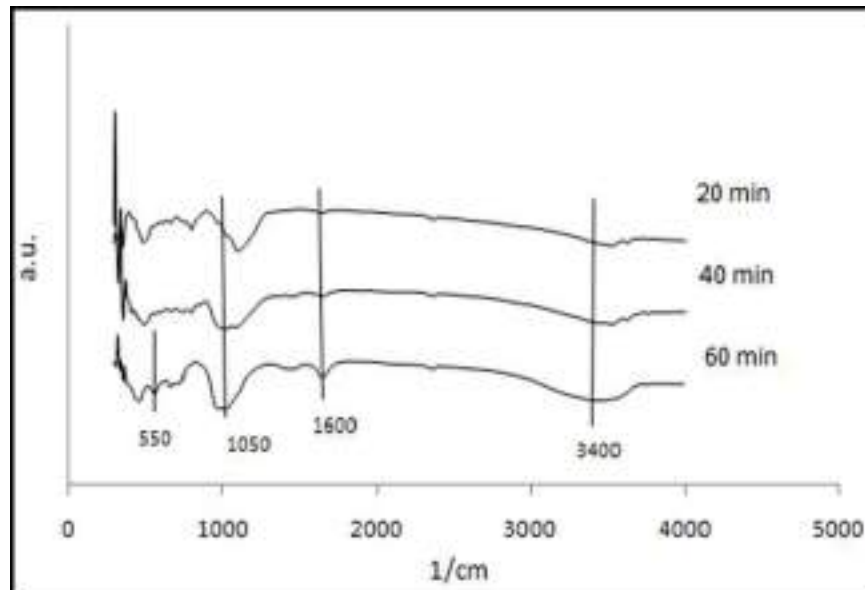
FTIR analysis was conducted to identify the functional group on the synthetic zeolite. The data were analyzed based on the Nicodom FTIR Spectra Libraries. These data were obtained from references, such as the general FTIR vibrational region  $300\text{-}400\text{ cm}^{-1}$  (vibrations of the external opening of the pores caused by breathing motion of the ring hole 12),  $420\text{-}500\text{ cm}^{-1}$  (Si-O/Al-O bending vibrations),  $500\text{-}650\text{ cm}^{-1}$  (double ring D4R/ D6R external vibration) which showed the formation of zeolite A,  $650\text{-}850\text{ cm}^{-1}$  (symmetric stretching vibrations of O-Si-O or O-Al-O),  $900\text{-}1250\text{ cm}^{-1}$  (asymmetric stretching vibrations of O-Si-O or O-Al-O),  $1600\text{-}1700\text{ cm}^{-1}$  (O-H bending vibration) which showed the presence of zeolitic water ( $\text{H}_2\text{O}$ ), and  $3400\text{-}3700\text{ cm}^{-1}$  (O-H stretching vibration of Si-OH) [21]. The FTIR spectra of zeolite synthesis which resulted at 3 variations was shown in Fig. 5, 6, and 7.



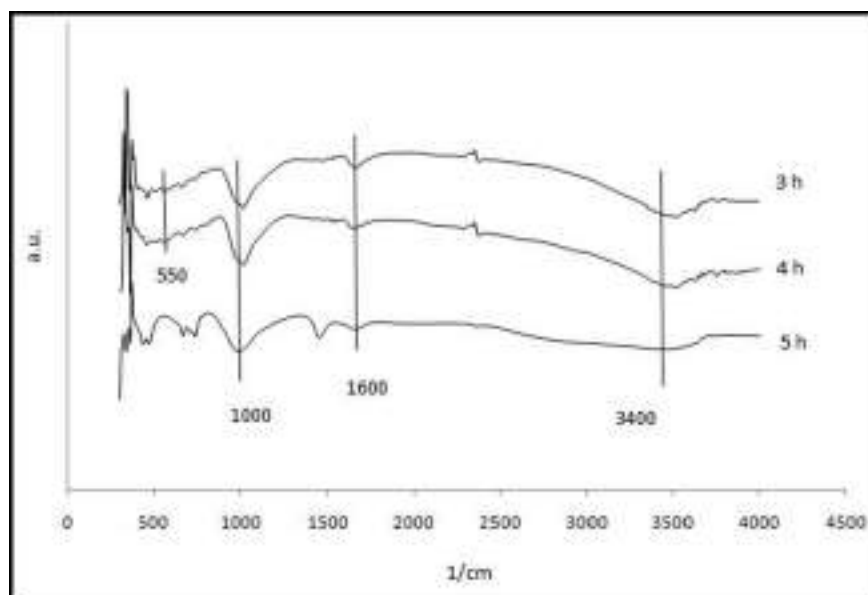
**Figure 5:** FTIR spectra of zeolite produced from microwave-hydrothermal synthesis for 2 hrs ageing



There were wavenumber  $555.5\text{ cm}^{-1}$  and  $563.21\text{ cm}^{-1}$  for 40 and 60 mins of 2 hrs ageing using the M-H method. The existence of absorption band in the region around  $500\text{--}650\text{ cm}^{-1}$  showed the double ring D4R or D6R. It was observed that zeolite A was only formed in variation for 40 and 60 mins of 2 h ageing using the M-H method. There was only wavenumber  $563.21\text{ cm}^{-1}$  for 60 mins of 5 hrs ageing with M-H. It was also found that zeolite A was only formed in variation for 60 mins of 5 hrs ageing with M-H. There were wavenumbers of  $555.5\text{ cm}^{-1}$  and  $555.5\text{ cm}^{-1}$  for 3 and 4 hrs of the 2 hrs ageing with C-H. The FTIR analysis was matched with the XRD test, that zeolite A was only formed in variation 3 and 4 hrs of the 2 hrs ageing with C-H.



**Figure 6:** FTIR spectra of zeolite produced from microwave-hydrothermal synthesis for 5 hrs ageing

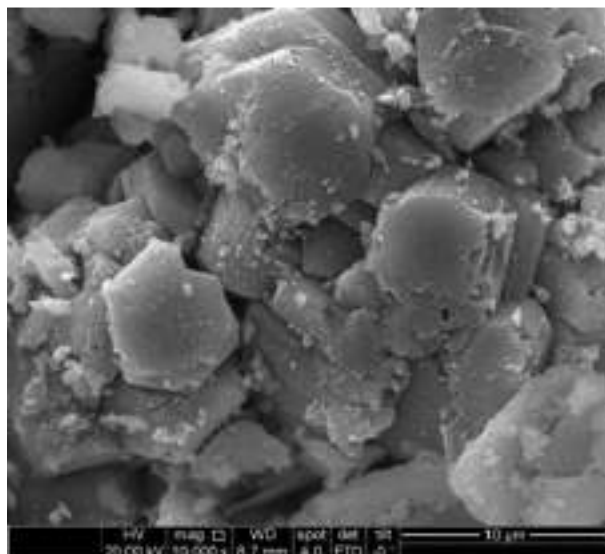


**Figure 7:** FTIR spectra of zeolite produced from conventional-hydrothermal synthesis for 2 hrs ageing

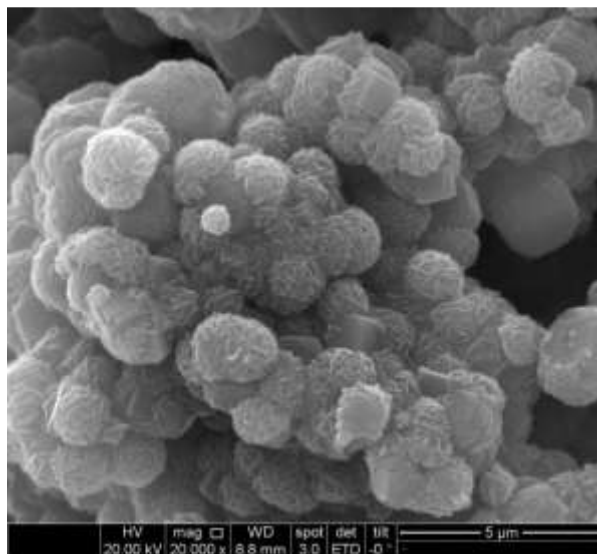
Scanning electron micrograph of the M-H process for 2 hrs ageing with holding time of 20, 40, and 60



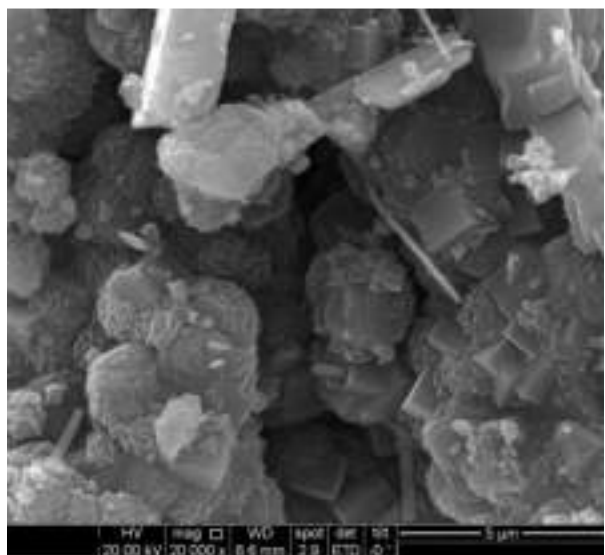
mins were shown in Fig. 8.a., 8.b., and 8.c, respectively. It was shown that on variation 20 mins, the formation of grain was not regular, while amorphous and zeolite A has not been formed yet. However, on variation 40 and 60 mins, zeolite A and sodalite were formed. Zeolite A has cubic while sodalite has spherical form with an array of long fibers that surrounded it. The same with M-H for the ageing of 2 and 5 hrs and the holding time of 20 mins. The zeolite A formed, as shown in Fig. 6.d. that the formation of grain was not regular or amorphous. The spherical form appeared on variation of 40 mins (Fig. 6.e), and showed that amorphous silica transformed into a crystal of zeolite. On variation of 60 mins (Fig. 6.f.), the image showed the formation of many cubes, in the form of zeolite A and sodalite, has spherical form with an array of long fibers that surround it. The grain size of zeolite A and sodalite we're approximately 1  $\mu\text{m}$ .



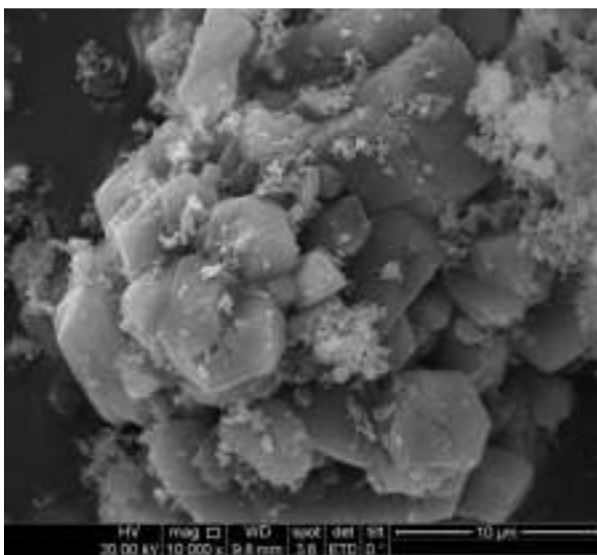
(a)



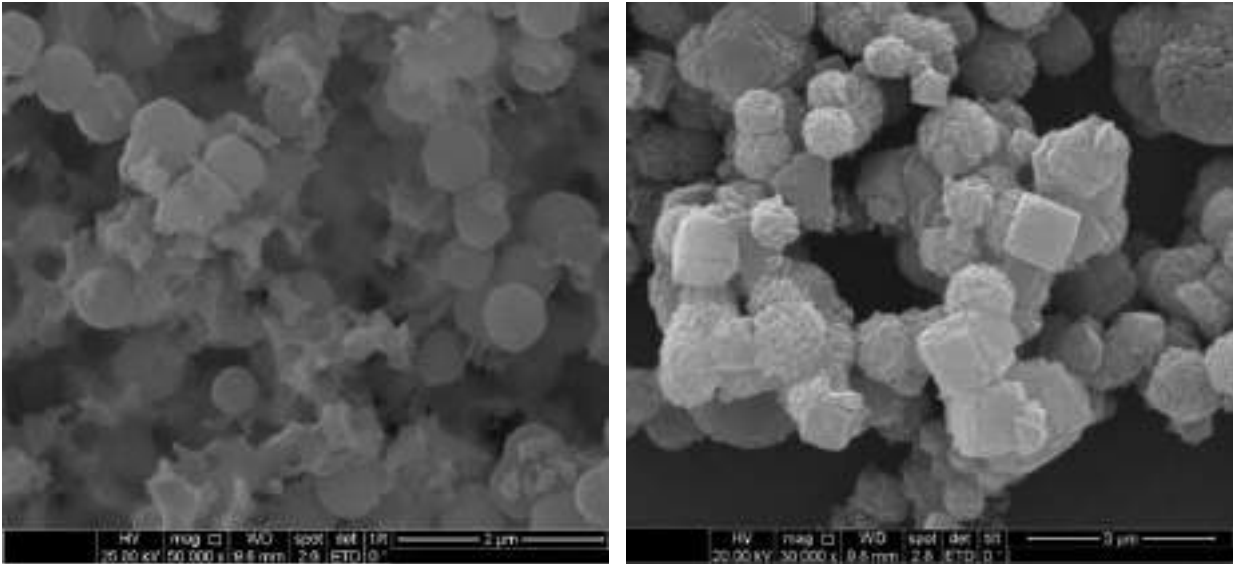
(b)



(c)



(d)

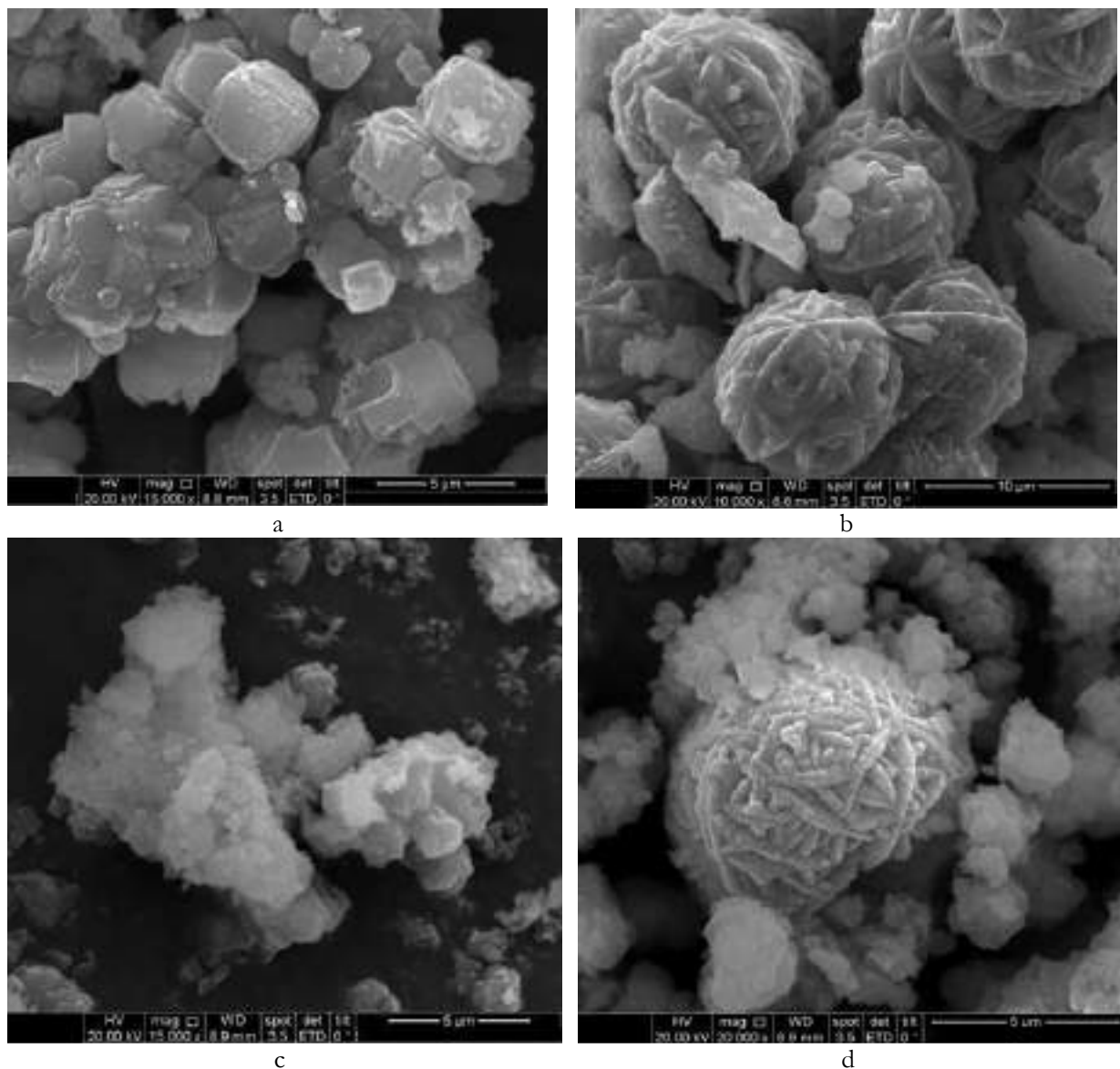


(e)

(f)

**Figure 8:** SEM image of synthetic zeolite for 2 hrs ageing with M-H (a) 20 min (b) 40 min (c) 60 min and 5 hrs (d) 20 min (e) 40 min (f) 60 min

The result of the SEM on the variation of 2 hrs ageing with C-H was shown in Fig. 9. On variation 3 hrs, the formation of zeolite A and sodalite with a grain size of about 5 µm and 10 µm, respectively were observed (Fig. 9.a. and Fig. 9.b.). Figure 9.a. showed that there was a cubic formation of zeolite A. Figure 9.b. showed sodalite phase. While Fig. 9.c. indicated that the formation of zeolite A and sodalite was not clear on variation 4 hrs, and only sodalite phase was observed, because zeolite A has been transformed into sodalite (Fig 9.d.). The M-H produced smaller and more homogeneous grain size of zeolite A and sodalite, due to faster and homogeneous heating compared to C-H. The formation of sodalite as a side product in the synthesis of NaA was explained by the inadequate mixing. The prolonged heating resulted in the dissolution and regrowth of crystals composition, e.g., when a NaA mixture moved into a HS range, eventually, all NaA were transformed into sodalite. However, when the synthesis mixture stayed in the NaA region, the only sodalite that nucleated was in the inhomogeneous pockets [33].



**Figure 9:** SEM image of synthetic zeolite 2 hrs ageing with C-H (a) 3 hrs zeolite A (b) 3 hrs sodalite (c) 4 hrs (d) 5 hrs

#### 4 Conclusions

Zeolite A was successfully synthesized from geothermal waste by conventional-hydrothermal (C-H) and microwave-hydrothermal (M-H) methods. This waste consists of 80.04 %  $\text{SiO}_2$  and 0.142 %  $\text{Al}_2\text{O}_3$ , while its silica content has high potential as an alternative source for synthesizing zeolite A. The rise of M-H and C-H time increased and decreased the crystallinity of zeolite A and sodalite, respectively. The fast crystallization observed using the M-H method affected the significant reduction in duration to 3 or 4 times shorter, producing smaller and more homogeneous crystal size compared to the C-H method.

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**Conflicts of Interest:** The authors declare no conflicts of interest regarding this study.

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## Zeolite A Synthesized from Geothermal Waste Using Conventional and Microwave Heating for the Hydrothermal Treatment

**Abstract:** Zeolite A has been successfully synthesized from geothermal waste with sodium aluminate and sodium silicate using conventional (C-H) and microwave heating (M-H) for the hydrothermal treatment. The products obtained for different aging times have been characterized using X-Ray Diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). It is shown that with the M-H process, zeolite can be formed at relatively low temperature (100 °C) in a relatively short time (40 min). The crystallization of zeolite A has been found to be generally promoted by an increase of aging and synthesis time; however, it has also been observed that relative long aging times can transform it into sodalite. Zeolite A produced through the M-H process generally displays a smaller and more homogeneous crystal size with respect to that obtained with the C-H method.

**Keywords:** Geothermal waste, microwave-hydrothermal, conventional-hydrothermal, zeolite A

### 1 Introduction

Geothermal energy is heat that generated or comes from the sub-surface of the earth. The geothermal energy produces heat and can be used as a resource in power plant generation. In the production process, wastes are produced (geothermal sludge and brine) in large quantities, and are the byproducts from power plants, in which the water and steam extracted from the underground are used to generate electricity [1,2].

Zeolites are crystals consisting of aluminate and silicate frameworks, with the ability to act as catalysts, adsorbents, etc. As a consequence of their properties, they have many potential applications in the fields of petrochemical reactions, water and gas purification [3-5]. Zeolite A is a type of zeolites, and due to its large ion exchange capacity, mechanical strength, and particular crystal shape, it is used in the substitution of sodium tripolyphosphate in the aspect of detergent and water softening.

In the synthesis of zeolite A, sodium silicate and sodium aluminate are the most commonly used Si and Al resources. One of the problems in zeolite synthesis is the unavailability and cost of raw material, specifically the silica source. In order to reduce the production cost of synthesized zeolite, many alternative materials, such as silica source have been proposed. Some natural minerals and wastes, such as clinoptilolite, oil shale, municipal solid, rice husk and coal fly ash were used to replace sodium silicate in the synthesis of zeolite A for cost-saving and environmental protection purposes [6-11]. Geothermal waste has high potential to be used as an alternative silica source for the synthesis of zeolite A, due to its silica contents. In previous study, by a conventional-hydrothermal process, geothermal waste was successfully converted into zeolite A and sodalite [12]. Colloidal silica extracted from geothermal fluid was synthesized to low Si/Al zeolite Y, with similarity characteristics compared to those prepared from a conventional silica sol or Ludox [13]. Hydrothermal process at 150 °C for 5 hours with 3 M of NaOH produced Zeolite X with octahedral crystal shape, having a specific surface area of 68.985 m<sup>2</sup>/gr and a pore volume of 0.109 cc/gr. The synthesized zeolite was successfully used as a catalyst for enhancing biohydrogen production [14, 15]. The colloidal silica extracted from geothermal fluids is used as silica source for zeolite synthesis [16]. The purity and yield of zeolite A synthesized from natural minerals and wastes using hydrothermal treatment were limited to the SiO<sub>2</sub> extraction. In order to increase the yield of SiO<sub>2</sub> and synthetic zeolite, several





methods, such as calcining, alkali, and acid activation were conducted to treat these raw materials before the synthesis process [12,17].

Several synthesis methods have been proposed for increasing the yield and purity of zeolite, besides conventional hydrothermal, some synthetic zeolites by microwave hydrothermal were produced. Also, numerous studies on the subject of microwave-hydrothermal (M-H) synthesis of zeolites have been published [9,18,19]. This research explained that the application of microwaves on zeolite synthesis, yield significant reduction in crystallization time due to faster and homogeneous heating, compared to conventional-hydrothermal (C-H) method. However, the fast temperature rise induced in the reacting solution by microwaves affects the nuclei formation, leading to the crystallization of undesired phases, or to the precipitation of amorphous solids [20,21]. The addition of seeds or ageing the solution were proved to bring a beneficial effect to nucleation in microwave synthesis of various zeolites [22]. Chu et al. (1998) was the first to show that microwave heating is used for the rapid synthesis of zeolites, and the crystallization of zeolite NaA was obtained in 12 min, contaminated with hydroxysodalite (HS), even when the mixture was aged for 2 hrs at room temperature before the M-H treatment [22]. Slangen et.al.(1997) obtained pure zeolite A in 5 mins crystallization, and after 20 hrs of ageing at room temperature. While the product with little hydroxysodalite was obtained in as short as 4 hrs of ageing [23]. In a laboratory scale, the microwave zeolite synthesis usually consists a batch reaction carried out in an autoclave made of a material transparent to microwaves, irradiated at 2.45 GHz in a multimodal oven cavity, similar to the customary household type [19, 25].

This study used calcined geothermal waste as silica sources in synthesizing zeolite A. This waste was added into alkali solution and aluminum source, followed by microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) method. The ageing effects and crystallization time, on the formation of zeolite A were also investigated.

## 2 Materials and Methods

Geothermal waste from geothermal power plant was dried under the sunlight and sieved with a 320-mesh sieving machine. The powder was calcined by burning at 850 °C for 3 hours at atmospheric condition using Carbolite furnace. Calcining process was carried out to burn unexpected or volatile materials. The chemical compositions of geothermal waste before and after calcining were characterized by atomic absorption spectroscopy (AAS) using Shimadzu type AA-6650 and the results were presented in the form of stable oxides as shown in Tab. 1.

The first step for zeolite synthesis was making sodium silicate. In this research, sodium silicate was made from 3 gr of geothermal waste mixed with 30 mL of NaOH 5 M. These mixtures were stirred at 100 °C for 20 min. Then, sodium aluminate was made from 20 g of NaOH 5 M dissolved in distilled water to yield 100 ml of 5 M NaOH, and then added 9 gr of Al(OH)<sub>3</sub> gradually, while stirring at 100 °C for 20 min. The two suspensions: 30 mL of sodium silicate and 30 mL of sodium aluminate were mixed and stirred using a magnetic stirrer at 200 rpm for 2 and 5 hours ageing time at room temperature. The moment the silica was added, it was taken as the beginning of ageing. This included the dissolution of silica in alumina solution [22], from this step resulted precursor gel for zeolite A synthesis.

**Table 1:** Chemical composition of geothermal powder

Compound	Before Calcining (wt. %)	After Calcining (wt,%)
Al <sub>2</sub> O <sub>3</sub>	0.055	0.142
Fe <sub>2</sub> O <sub>3</sub>	0.192	0.451
Na <sub>2</sub> O <sub>3</sub>	0.609	0.760
SiO <sub>2</sub>	49.100	80.043



A household-type microwave oven 2.45 GHz (Panasonic NN-SM320M) with maximum output power 450 Watt was used for microwave synthesis. For measuring the temperature of the process, the thermocouple was inserted into the microwave. The precursor gel was poured into a Teflon(R) box and placed into the microwave and heated at 100°C for 20, 40, and 60 min. The Teflon(R) autoclave with controllable heating was used for conventional hydrothermal process. This was performed by pouring the precursor gel into the Teflon(R) autoclave and heated until 100 °C with holding time 3, 4, and 5 hours. The synthesized products were washed with aquabidest and filtered with whatmann 42 paper to separate between solid and filtrate. The solid powder was dried in the oven at 80 °C for 4 hours. The powders were analyzed by Rigaku X-ray diffractometer using CuK $\alpha$  radiation (40 kV, 30 mA), 8201PC Shimadzu FTIR (Fourier Transform Infra-Red) and JEOL JSM 6300 SEM (Scanning Electron Microscope).

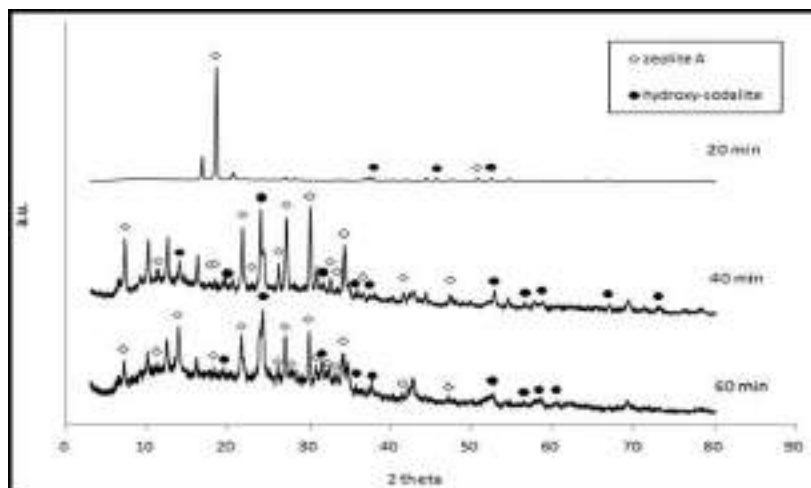
### 3 Results and Discussions

Tab. 1 shows that the geothermal powder before calcining contains 49.10% SiO<sub>2</sub>, and after, it increases up to 80.04 %. Munfarida et. al. has reported that using EDX analysis geothermal waste form power plant has SiO<sub>2</sub> containing 35.09 % and Al<sub>2</sub>O<sub>3</sub> about 0.05 % [26]. Calcining process causes unexpected and volatile materials to burned out. While the calcined geothermal waste produced Si/Al ratio 1.79 as shown on Table 2. This ratio allows the formation of zeolite A, which according to the literature that this product has a ratio of Si/Al ranging from 1-3.5 [21]. Sulardjaka et.al (2014) reported that the geothermal powder before calcining contained silica in amorphous form, there was no dominant peak from the diffractogram. However, the peaks were found at 21.91 and 20.88 in the calcined geothermal powder. This indicated that there was transformation of amorphous silica into primary cristobalite [12]. During the calcining process until 850 °C for 3 hours, some of the silica transformed into cristobalite phase, and the amorphous silica phase was still dominant [27,28]. SiO<sub>2</sub> in amorphous form in geothermal waste has potential as a silica resources for zeolite synthesis.

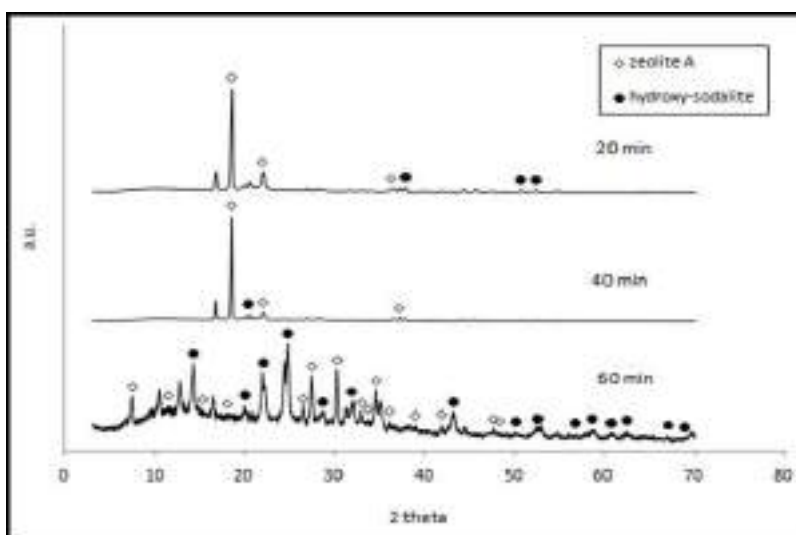
**Table 2:** Si/Al ratio of synthetic mixture

Sample	Element	Average (wt. %)
Precursor gel	Al	5.86
	Si	10.48

XRD diffraction pattern of synthesized products from microwave-hydrothermal of geothermal waste for 2 hrs and 5 hrs ageing time were shown at Fig. 1 and 2 respectively. The phases produced from conventional-hydrothermal were shown in Fig. 3. The diffractogram pattern as shown in Fig. 1, 2, and 3, correlated with that from JCPDS data number 11-0401 (hydroxy-sodalite) and 31-1269 (zeolite A). This showed that the synthetic zeolite in all the variation contained crystal of zeolite A and sodalite. During the microwave-hydrothermal for 2 h ageing, holding time for 20 mins, phase zeolite A became the dominant. While increasing the holding time to 40 and 60 mins, the zeolite A also increased and sodalite phase was formed. X-Ray diffraction of microwave-hydrothermal of geothermal waste for 5 hrs ageing showed that at the ageing of 20 and 40 mins, zeolite A phase was dominant. The rise of holding time to 60 mins, increased the zeolite A and produced sodalite phase.



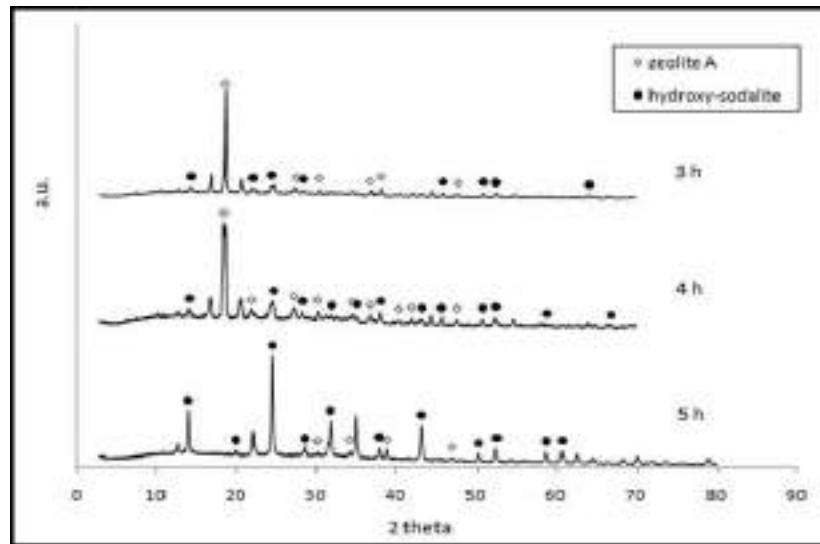
**Figure 1:** X-Ray diffraction of microwave-hydrothermal of geothermal waste for 2 hrs ageing with the variation of holding time



**Figure 2:** X-Ray diffraction of microwave-hydrothermal of geothermal waste for 5 hrs ageing with the variation of holding time

Fig. 3 showed X-Ray diffraction of conventional-hydrothermal of geothermal waste for 2 hrs ageing with 3, 4, 5 hours holding time. At the holding time of 3 hours, zeolite A and less sodalite phase were produced. The rise of holding time, increased zeolite A and sodalite phases. The holding time for 5 hours hydroxy-sodalite phase was dominant. The microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) of geothermal waste produced synthetic zeolite. Zeolites A and sodalite were produced in all of the variation of microwave-hydrothermal processes. The increasing M-H time, elevated the production of zeolite A and sodalite. However, the increasing C-H time, decreased the zeolite A phase and raised that of sodalite. In zeolite A synthesis, the formation of building units and the nucleation of zeolite with it, was followed by crystal growth by adsorption of the units on the surface of the zeolite nuclei and crystal. At the longer holding time, the impurity phase of zeolite A was formed. There has been a transformation from zeolite A  $\rightarrow$  sodalite. At the surface-to-core extension of crystallization, sodalite nanoplates were crystallized within the amorphous cores of zeolite A. At the longer holding time, sodalite nanoplates increased in size and breaking the cubic shells of zeolite A in the process. This led to the phase

transformation from zeolite A to sodalite [28-30].



**Figure 3.** X-Ray diffraction of conventional-hydrothermal of geothermal waste for 2 hrs ageing with variation of holding time

The average of crystal grain size of synthesized zeolites was determined from the results of XRD graphs, this was calculated using Scherer formula [31, 32].

$$L = \frac{57.3 \times k \times \gamma}{\beta \times \cos \theta} \quad (1)$$

Where:

L = crystal grain size (nm),

k = oxide constant (0.94),

$\lambda$  = X-ray wavelength (1.5406 Å),

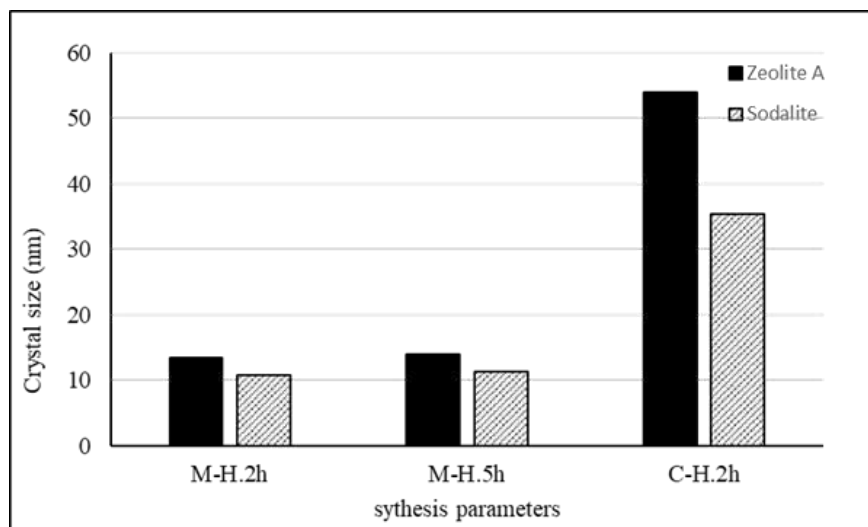
$\beta$  = the value of FWHM (deg),

$\theta$  = angle of crystal diffraction peak position (deg),

57.3 = correction factor from degree to radian.

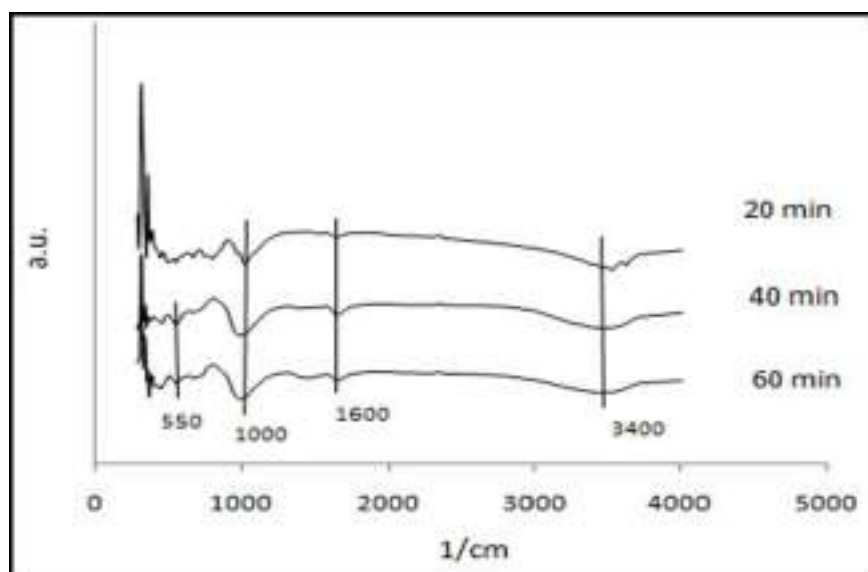
The results of the crystal grain size calculation using Scherer formula was shown in Figure 4. The crystal size of zeolite A produced from M-H were 13.43 nm (ageing 2 hrs) and 14 nm (ageing 5 hrs). The C-H with 2 hrs ageing produced zeolite A with crystal size of 53.94 nm, and sodalite of 35.4 nm. The sodalite with crystal size of 10.78 nm (ageing 2 hrs) and 11.38 nm (ageing 5 hrs) were also formed from M-H. The M-H produced smaller and more homogeneous crystal size of zeolite A and sodalite, due to faster and homogeneous heating compared to the C-H. Ageing time with variation of 2 and 5 hrs on the M-H method affected nucleation and crystallization of synthetic zeolite. The ageing of precursor gels resulted in the acceleration of the crystallization and crystal size diminution of the synthesis product. This ageing process directly influenced the concentration and number of formed nuclei [33]. The fast crystallization on M-H method affected the significant reduction of its time, 3 or 4 times, shorter than that of C-H method. It was also observed that the time and temperature of microwave heating had significant effects on the prepared zeolite particles. The shortening of synthesis times in microwave heating was caused by two different mechanisms, i.e., the rapid heat-up of the sample and a better heat transfer which resulted in the

rapid and thorough heating of the synthesis mixture. This easily resulted in rapid and vivid heating of the synthesis mixture and effect a faster crystallization [34, 35].



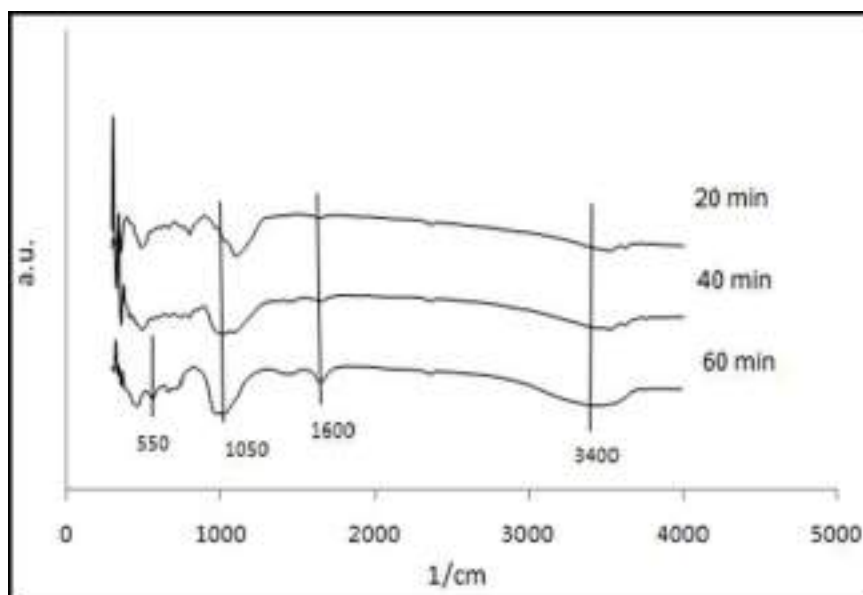
**Figure 4:** Crystal size of zeolite A and hydroxy-sodalite

FTIR analysis was conducted to identify the functional group on the synthetic zeolite. The data were analyzed based on the Nicodom FTIR Spectra Libraries. These data were obtained from references, such as the general FTIR vibrational region  $300\text{-}400\text{ cm}^{-1}$  (vibrations of the external opening of the pores caused by breathing motion of the ring hole 12),  $420\text{-}500\text{ cm}^{-1}$  (Si-O/Al-O bending vibrations),  $500\text{-}650\text{ cm}^{-1}$  (double ring D4R/ D6R external vibration) which showed the formation of zeolite A,  $650\text{-}850\text{ cm}^{-1}$  (symmetric stretching vibrations of O-Si-O or O-Al-O),  $900\text{-}1250\text{ cm}^{-1}$  (asymmetric stretching vibrations of O-Si-O or O-Al-O),  $1600\text{-}1700\text{ cm}^{-1}$  (O-H bending vibration) which showed the presence of zeolitic water ( $\text{H}_2\text{O}$ ), and  $3400\text{-}3700\text{ cm}^{-1}$  (O-H stretching vibration of Si-OH) [21]. The FTIR spectra of zeolite synthesis which resulted at 3 variations was shown in Fig. 5, 6, and 7.

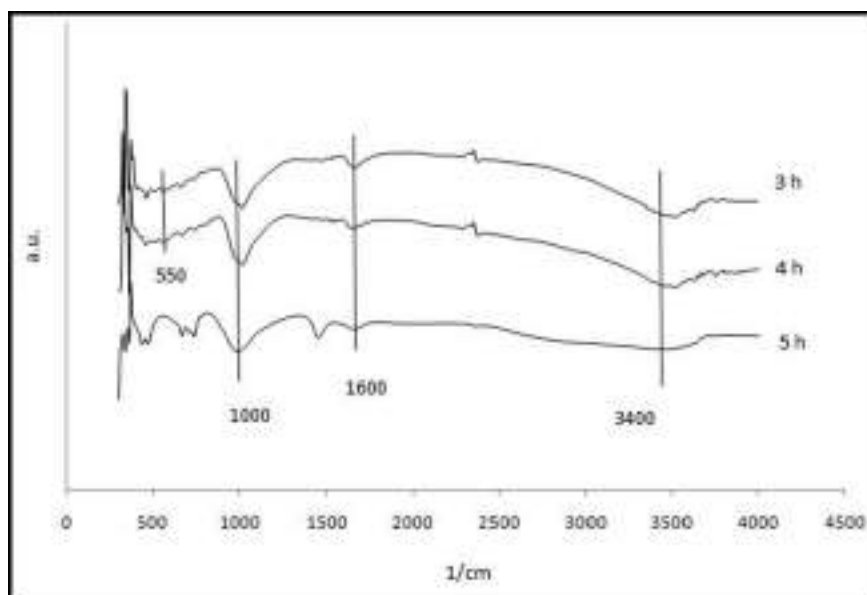


**Figure 5:** FTIR spectra of zeolite produced from microwave-hydrothermal synthesis for 2 hrs ageing

There were wavenumber  $555.5\text{ cm}^{-1}$  and  $563.21\text{ cm}^{-1}$  for 40 and 60 mins of 2 hrs ageing using the M-H method. The existence of absorption band in the region around  $500\text{--}650\text{ cm}^{-1}$  showed the double ring D4R or D6R. It was observed that zeolite A was only formed in variation for 40 and 60 mins of 2 h ageing using the M-H method. There was only wavenumber  $563.21\text{ cm}^{-1}$  for 60 mins of 5 hrs ageing with M-H. It was also found that zeolite A was only formed in variation for 60 mins of 5 hrs ageing with M-H. There were wavenumbers of  $555.5\text{ cm}^{-1}$  and  $555.5\text{ cm}^{-1}$  for 3 and 4 hrs of the 2 hrs ageing with C-H. The FTIR analysis was matched with the XRD test, that zeolite A was only formed in variation 3 and 4 hrs of the 2 hrs ageing with C-H.



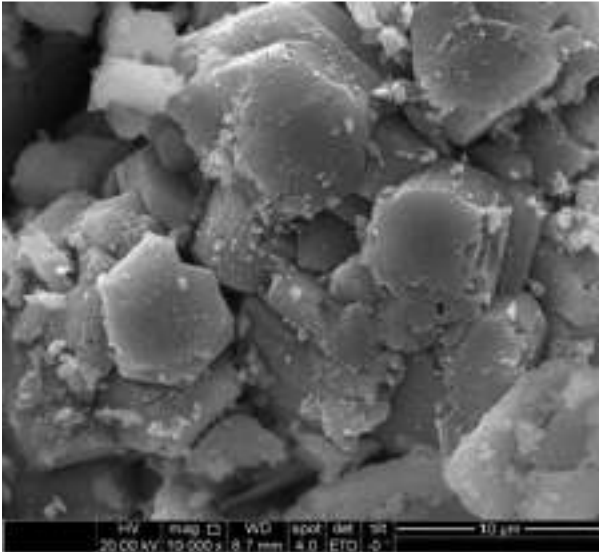
**Figure 6:** FTIR spectra of zeolite produced from microwave-hydrothermal synthesis for 5 hrs ageing



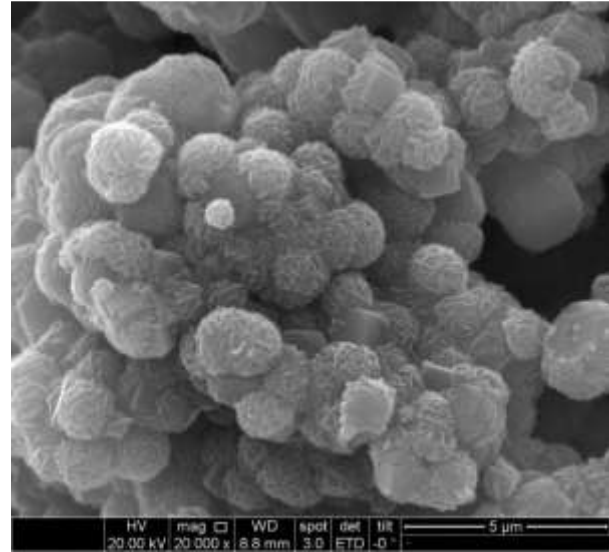
**Figure 7:** FTIR spectra of zeolite produced from conventional-hydrothermal synthesis for 2 hrs ageing

Scanning electron micrograph of the M-H process for 2 hrs ageing with holding time of 20, 40, and 60

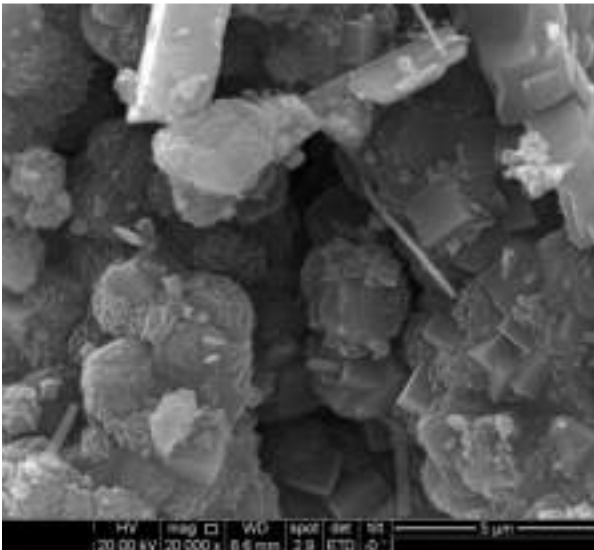
mins were shown in Fig. 8.a., 8.b., and 8.c, respectively. It was shown that on variation 20 mins, the formation of grain was not regular, while amorphous and zeolite A has not been formed yet. However, on variation 40 and 60 mins, zeolite A and sodalite were formed. Zeolite A has cubic while sodalite has spherical form with an array of long fibers that surrounded it. The same with M-H for the ageing of 2 and 5 hrs and the holding time of 20 mins. The zeolite A formed, as shown in Fig. 6.d. that the formation of grain was not regular or amorphous. The spherical form appeared on variation of 40 mins (Fig. 6.e), and showed that amorphous silica transformed into a crystal of zeolite. On variation of 60 mins (Fig. 6.f.), the image showed the formation of many cubes, in the form of zeolite A and sodalite, has spherical form with an array of long fibers that surround it. The grain size of zeolite A and sodalite we're approximately 1  $\mu\text{m}$ .



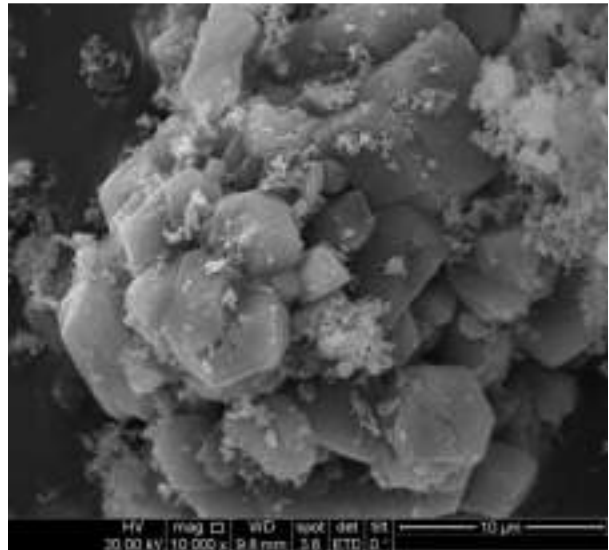
(a)



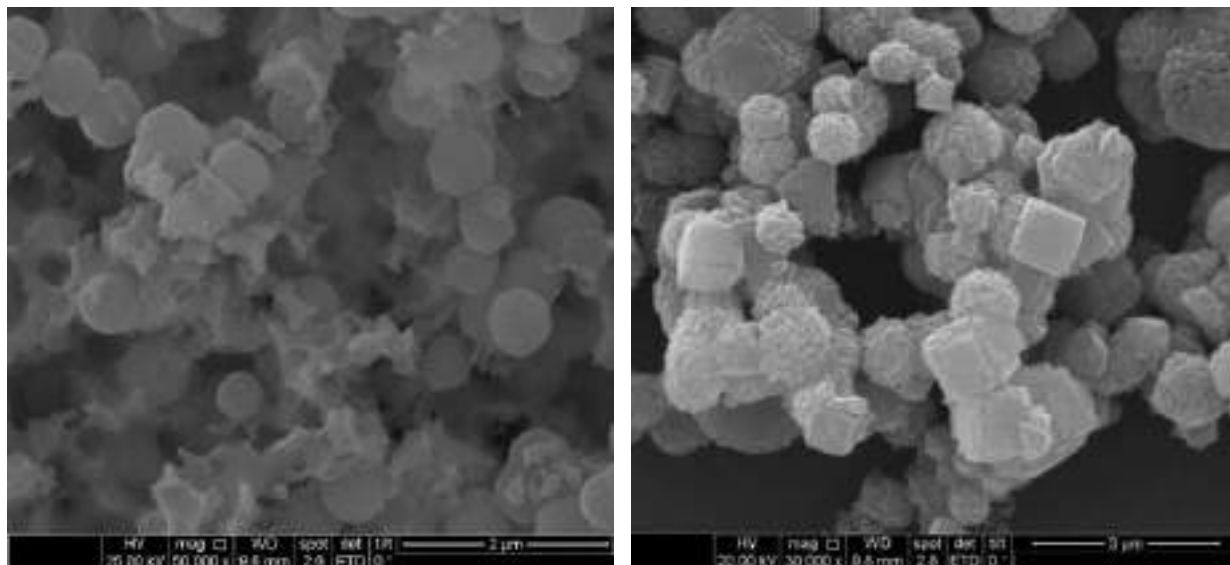
(b)



(c)



(d)

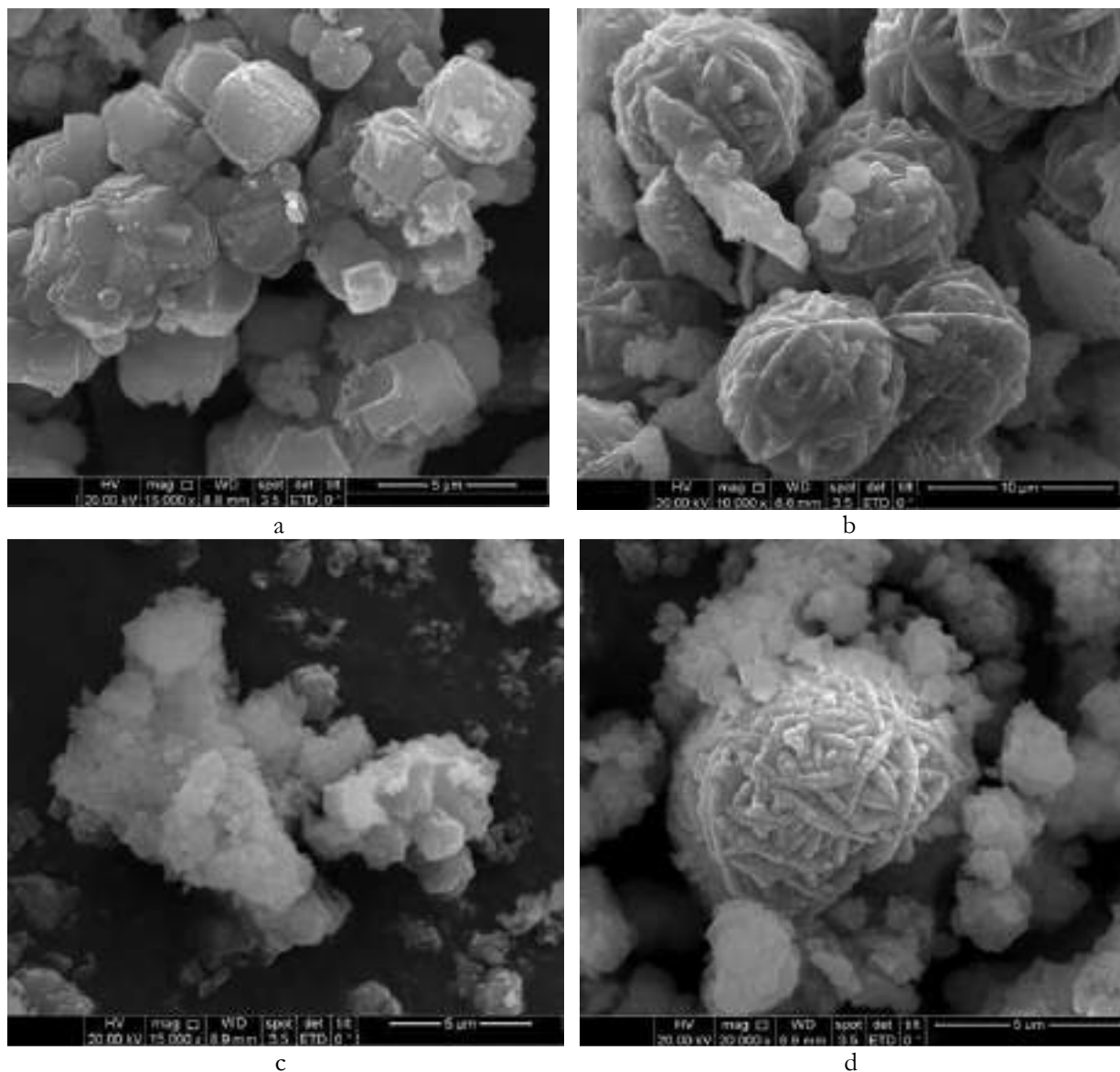


(e)

(f)

**Figure 8:** SEM image of synthetic zeolite for 2 hrs ageing with M-H (a) 20 min (b) 40 min (c) 60 min and 5 hrs (d) 20 min (e) 40 min (f) 60 min

The result of the SEM on the variation of 2 hrs ageing with C-H was shown in Fig. 9. On variation 3 hrs, the formation of zeolite A and sodalite with a grain size of about 5  $\mu\text{m}$  and 10  $\mu\text{m}$ , respectively were observed (Fig. 9.a. and Fig. 9.b.). Figure 9.a. showed that there was a cubic formation of zeolite A. Figure 9.b. showed sodalite phase. While Fig. 9.c. indicated that the formation of zeolite A and sodalite was not clear on variation 4 hrs, and only sodalite phase was observed, because zeolite A has been transformed into sodalite (Fig 9.d.). The M-H produced smaller and more homogeneous grain size of zeolite A and sodalite, due to faster and homogeneous heating compared to C-H. The formation of sodalite as a side product in the synthesis of NaA was explained by the inadequate mixing. The prolonged heating resulted in the dissolution and regrowth of crystals composition, e.g., when a NaA mixture moved into a HS range, eventually, all NaA were transformed into sodalite. However, when the synthesis mixture stayed in the NaA region, the only sodalite that nucleated was in the inhomogeneous pockets [33].



**Figure 9:** SEM image of synthetic zeolite 2 hrs ageing with C-H (a) 3 hrs zeolite A (b) 3 hrs sodalite (c) 4 hrs (d) 5 hrs

#### 4 Conclusions

Zeolite A was successfully synthesized from geothermal waste by conventional-hydrothermal (C-H) and microwave-hydrothermal (M-H) methods. This waste consists of 80.04 %  $\text{SiO}_2$  and 0.142 %  $\text{Al}_2\text{O}_3$ , while its silica content has high potential as an alternative source for synthesizing zeolite A. The rise of M-H and C-H time increased and decreased the crystallinity of zeolite A and sodalite, respectively. The fast crystallization observed using the M-H method affected the significant reduction in duration to 3 or 4 times shorter, producing smaller and more homogeneous crystal size compared to the C-H method.

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**Conflicts of Interest:** The authors declare no conflicts of interest regarding this study.

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ARTICLE

# Zeolite A Synthesized from Geothermal Waste Using Conventional and Microwave Heating for the Hydrothermal Treatment

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## ABSTRACT

Zeolite A has been successfully synthesized from geothermal waste with natrium aluminate and natrium silicate using conventional (C-H) and microwave heating (M-H) for the hydrothermal treatment. The products obtained for different aging times have been characterized using X-Ray Diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). It is shown that with the M-H process, zeolite can be formed at relatively low temperature (100°C) in a relatively short time (40 min). The crystallization of zeolite A has been found to be generally promoted by an increase of aging and synthesis time; however, it has also been observed that relative long aging times can transform it into sodalite. Zeolite A produced through the M-H process generally displays a smaller and more homogeneous crystal size with respect to that obtained with the C-H method.

## KEYWORDS

Geothermal waste; microwave-hydrothermal; conventional-hydrothermal; zeolite A

## 1 Introduction

Geothermal energy is heat that generated or comes from the sub-surface of the earth. The geothermal energy produces heat and can be used as a resource in power plant generation. In the production process, wastes are produced (geothermal sludge and brine) in large quantities, and are the byproducts from power plants, in which the water and steam extracted from the underground are used to generate electricity [1,2].

Zeolites are crystals consisting of aluminate and silicate frameworks, with the ability to act as catalysts, adsorbents, etc. As a consequence of their properties, they have many potential applications in the fields of petrochemical reactions, water and gas purification [3–5]. Zeolite A is a type of zeolites, and due to its large ion exchange capacity, mechanical strength, and particular crystal shape, it is used in the substitution of sodium tripolyphosphate in the aspect of detergent and water softening.

In the synthesis of zeolite A, sodium silicate and sodium aluminate are the most commonly used Si and Al resources. One of the problems in zeolite synthesis is the unavailability and cost of raw material, specifically the silica source. In order to reduce the production cost of synthesized zeolite, many alternative materials, such as silica source have been proposed. Some natural minerals and wastes, such as clinoptilolite, oil shale, municipal solid, rice husk and coal fly ash were used to replace sodium silicate in the synthesis of zeolite A for cost-saving and environmental protection purposes [6–11]. Geothermal



waste has high potential to be used as an alternative silica source for the synthesis of zeolite A, due to its silica contents. In previous study, by a conventional-hydrothermal process, geothermal waste was successfully converted into zeolite A and sodalite [12]. Colloidal silica extracted from geothermal fluid was synthesized to low Si/Al zeolite Y, with similarity characteristics compared to those prepared from a conventional silica sol or Ludox [13]. Hydrothermal process at 150°C for 5 h with 3 M of NaOH produced Zeolite X with octahedral crystal shape, having a specific surface area of 68.985 m<sup>2</sup>/gr and a pore volume of 0.109 cc/gr. The synthesized zeolite was successfully used as a catalyst for enhancing biohydrogen production [14,15]. The colloidal silica extracted from geothermal fluids is used as silica source for zeolite synthesis [16]. The purity and yield of zeolite A synthesized from natural minerals and wastes using hydrothermal treatment were limited to the SiO<sub>2</sub> extraction. In order to increase the yield of SiO<sub>2</sub> and synthetic zeolite, several methods, such as calcining, alkali, and acid activation were conducted to treat these raw materials before the synthesis process [12,17].

Several synthesis methods have been proposed for increasing the yield and purity of zeolite, besides conventional hydrothermal, some synthetic zeolites by microwave hydrothermal were produced. Also, numerous studies on the subject of microwave-hydrothermal (M-H) synthesis of zeolites have been published [9,18,19]. This research explained that the application of microwaves on zeolite synthesis, yield significant reduction in crystallization time due to faster and homogeneous heating, compared to conventional-hydrothermal (C-H) method. However, the fast temperature rise induced in the reacting solution by microwaves affects the nuclei formation, leading to the crystallization of undesired phases, or to the precipitation of amorphous solids [20,21]. The addition of seeds or ageing the solution were proved to bring a beneficial effect to nucleation in microwave synthesis of various zeolites [22]. Chu et al. [23] was the first to show that microwave heating is used for the rapid synthesis of zeolites, and the crystallization of zeolite NaA was obtained in 12 min, contaminated with hydroxysodalite (HS), even when the mixture was aged for 2 h at room temperature before the M-H treatment. Slangen et al. [24] obtained pure zeolite A in 5 mins crystallization, and after 20 h of ageing at room temperature. While the product with little hydroxysodalite was obtained in as short as 4 h of ageing. In a laboratory scale, the microwave zeolite synthesis usually consists a batch reaction carried out in an autoclave made of a material transparent to microwaves, irradiated at 2.45 GHz in a multimodal oven cavity, similar to the customary household type [19,25].

This study used calcined geothermal waste as silica sources in synthesizing zeolite A. This waste was added into alkali solution and aluminum source, followed by microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) method. The ageing effects and crystallization time, on the formation of zeolite A were also investigated.

## 2 Materials and Methods

Geothermal waste from geothermal power plant was dried under the sunlight and sieved with a 320-mesh sieving machine. The powder was calcined by burning at 850°C for 3 h at atmospheric condition using Carbolite furnace. Calcining process was carried out to burn unexpected or volatile materials. The chemical compositions of geothermal waste before and after calcining were characterized by atomic absorption spectroscopy (AAS) using Shimadzu type AA-6650 and the results were presented in the form of stable oxides as shown in Tab. 1.

The first step for zeolite synthesis was making sodium silicate. In this research, sodium silicate was made from 3 gr of geothermal waste mixed with 30 mL of NaOH 5 M. These mixtures were stirred at 100°C for 20 min. Then, sodium aluminate was made from 20 g of NaOH 5 M dissolved in distilled water to yield 100 ml of 5 M NaOH, and then added 9 gr of Al(OH)<sub>3</sub> gradually, while stirring at 100°C for 20 min. The two suspensions: 30 mL of sodium silicate and 30 mL of sodium aluminate were mixed and stirred using a magnetic stirrer at 200 rpm for 2 h and 5 h ageing time at room temperature. The moment the silica

was added, it was taken as the beginning of ageing. This included the dissolution of silica in alumina solution [22], from this step resulted precursor gel for zeolite A synthesis.

Table 1: Chemical composition of geothermal powder

Compound	Before Calcining (wt. %)	After Calcining (wt.%)
Al <sub>2</sub> O <sub>3</sub>	0.055	0.142
Fe <sub>2</sub> O <sub>3</sub>	0.192	0.451
Na <sub>2</sub> O <sub>3</sub>	0.609	0.760
SiO <sub>2</sub>	49.100	80.043

A household-type microwave oven 2.45 GHz (Panasonic NN-SM320M) with maximum output power 450 Watt was used for microwave synthesis. For measuring the temperature of the process, the thermocouple was inserted into the microwave. The precursor gel was poured into a Teflon(R) box and placed into the microwave and heated at 100°C for 20, 40, and 60 min. The Teflon(R) autoclave with controllable heating was used for conventional hydrothermal process. This was performed by pouring the precursor gel into the Teflon(R) autoclave and heated until 100°C with holding time 3 h, 4 h, and 5 h. The synthesized products were washed with aquabidest and filtered with whatmann 42 paper to separate between solid and filtrate. The solid powder was dried in the oven at 80°C for 4 h. The powders were analyzed by Rigaku X-ray diffractometer using CuK $\alpha$  radiation (40 kV, 30 mA), 8201PC Shimadzu FTIR (Fourier Transform Infra-Red) and JEOL JSM 6300 SEM (Scanning Electron Microscope).

### 3 Results and Discussions

Tab. 1 shows that the geothermal powder before calcining contains 49.10% SiO<sub>2</sub>, and after, it increases up to 80.04 %. Munfarida et. al. has reported that using EDX analysis geothermal waste form power plant has SiO<sub>2</sub> containing 35.09% and Al<sub>2</sub>O<sub>3</sub> about 0.05% [26]. Calcining process causes unexpected and volatile materials to burned out. While the calcined geothermal waste produced Si/Al ratio 1.79 as shown on Tab. 2. This ratio allows the formation of zeolite A, which according to the literature that this product has a ratio of Si/Al ranging from 1–3.5 [21]. Sulardjaka et al. [12] reported that the geothermal powder before calcining contained silica in amorphous form, there was no dominant peak from the diffractogram. However, the peaks were found at 21.91 and 20.88 in the calcined geothermal powder. This indicated that there was transformation of amorphous silica into primary cristobalite. During the calcining process until 850°C for 3 h, some of the silica transformed into cristobalite phase, and the amorphous silica phase was still dominant [27,28]. SiO<sub>2</sub> in amorphous form in geothermal waste has potential as a silica resources for zeolite synthesis.

Table 2: Si/Al ratio of synthetic mixture

Sample	Element	Average (wt. %)
Precursor gel	Al	5.86
	Si	10.48

XRD diffraction pattern of synthesized products from microwave-hydrothermal of geothermal waste for 2 h and 5 h ageing time were shown at Figs. 1 and 2 respectively. The phases produced from conventional-hydrothermal were shown in Fig. 3. The diffractogram pattern as shown in Figs. 1, 2, and 3, correlated with that from JCPDS data number 11-0401 (hydroxy-sodalite) and 31-1269 (zeolite A). This showed that the

synthetic zeolite in all the variation contained crystal of zeolite A and sodalite. During the microwave-hydrothermal for 2 h ageing, holding time for 20 mins, phase zeolite A became the dominant. While increasing the holding time to 40 and 60 mins, the zeolite A also increased and sodalite phase was formed. X-Ray diffraction of microwave-hydrothermal of geothermal waste for 5 h ageing showed that at the ageing of 20 and 40 mins, zeolite A phase was dominant. The rise of holding time to 60 mins, increased the zeolite A and produced sodalite phase.

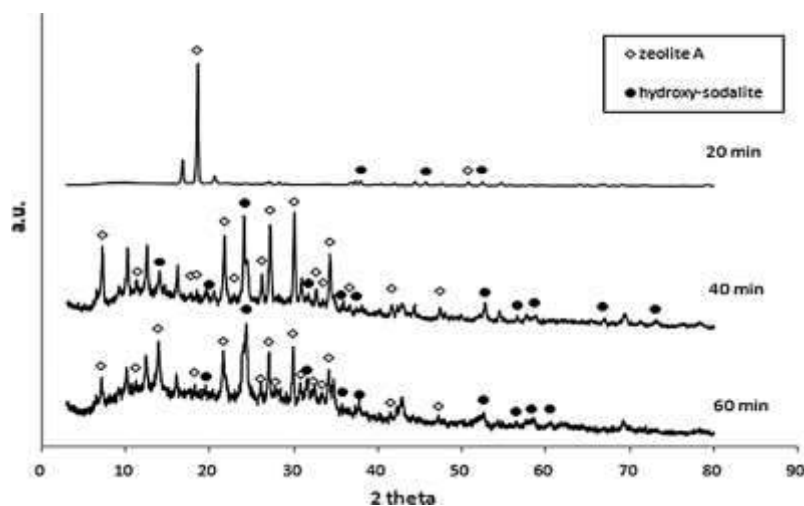


Figure 1: X-Ray diffraction of microwave-hydrothermal of geothermal waste for 2 h ageing with the variation of holding time

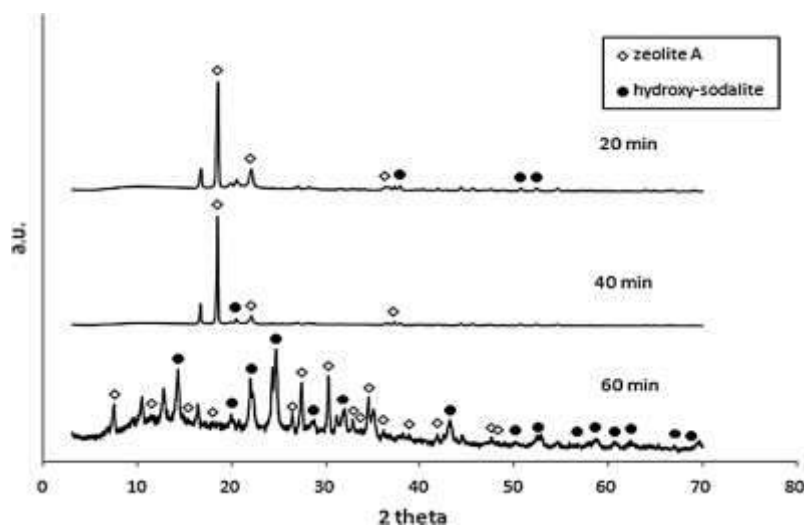


Figure 2: X-Ray diffraction of microwave-hydrothermal of geothermal waste for 5 h ageing with the variation of holding time

Fig. 3 showed X-Ray diffraction of conventional-hydrothermal of geothermal waste for 2 h ageing with 3 h, 4 h, 5 h holding time. At the holding time of 3 h, zeolite A and less sodalite phase were produced. The rise of holding time, increased zeolite A and sodalite phases. The holding time for 5 h hydroxy-sodalite phase



was dominant. The microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) of geothermal waste produced synthetic zeolite. Zeolites A and sodalite were produced in all of the variation of microwave-hydrothermal processes. The increasing M-H time, elevated the production of zeolite A and sodalite. However, the increasing C-H time, decreased the zeolite A phase and raised that of sodalite. In zeolite A synthesis, the formation of building units and the nucleation of zeolite with it, was followed by crystal growth by adsorption of the units on the surface of the zeolite nuclei and crystal. At the longer holding time, the impurity phase of zeolite A was formed. There has been a transformation from zeolite A  $\rightarrow$  sodalite. At the surface-to-core extension of crystallization, sodalite nanoplates were crystallized within the amorphous cores of zeolite A. At the longer holding time, sodalite nanoplates increased in size and breaking the cubic shells of zeolite A in the process. This led to the phase transformation from zeolite A to sodalite [28–30].

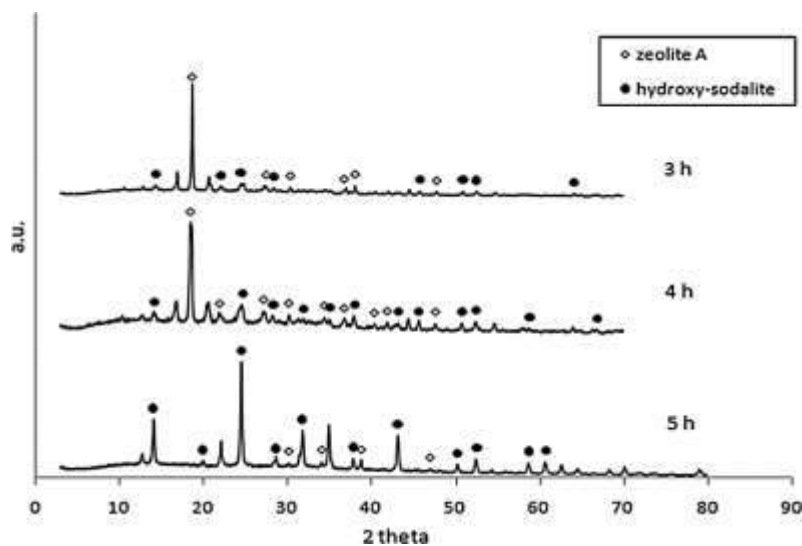


Figure 3: X-Ray diffraction of conventional-hydrothermal of geothermal waste for 2 h ageing with variation of holding time

The average of crystal grain size of synthesized zeolites was determined from the results of XRD graphs, this was calculated using Scherer formula [31,32].

$$L \approx \frac{57.3 \times k \times \lambda}{\beta \times \cos \theta} \quad (1)$$

where:

$L$  = crystal grain size (nm),

$k$  = oxide constant (0.94),

$\lambda$  = X-ray wavelength (1.5406 Å),

$\beta$  = the value of FWHM (deg),

$\theta$  = angle of crystal diffraction peak position (deg),

57.3 = correction factor from degree to radian.

The results of the crystal grain size calculation using Scherer formula was shown in Fig. 4. The crystal size of zeolite A produced from M-H were 13.43 nm (ageing 2 h) and 14 nm (ageing 5 h). The C-H with 2 h



ageing produced zeolite A with crystal size of 53.94 nm, and sodalite of 35.4 nm. The sodalite with crystal size of 10.78 nm (ageing 2 h) and 11.38 nm (ageing 5 h) were also formed from M-H. The M-H produced smaller and more homogeneous crystal size of zeolite A and sodalite, due to faster and homogeneous heating compared to the C-H. Ageing time with variation of 2 h and 5 h on the M-H method affected nucleation and crystallization of synthetic zeolite. The ageing of precursor gels resulted in the acceleration of the crystallization and crystal size diminution of the synthesis product. This ageing process directly influenced the concentration and number of formed nuclei [33]. The fast crystallization on M-H method affected the significant reduction of its time, 3 or 4 times, shorter than that of C-H method. It was also observed that the time and temperature of microwave heating had significant effects on the prepared zeolite particles. The shortening of synthesis times in microwave heating was caused by two different mechanisms, i.e., the rapid heat-up of the sample and a better heat transfer which resulted in the rapid and thorough heating of the synthesis mixture. This easily resulted in rapid and vivid heating of the synthesis mixture and effect a faster crystallization [34,35].

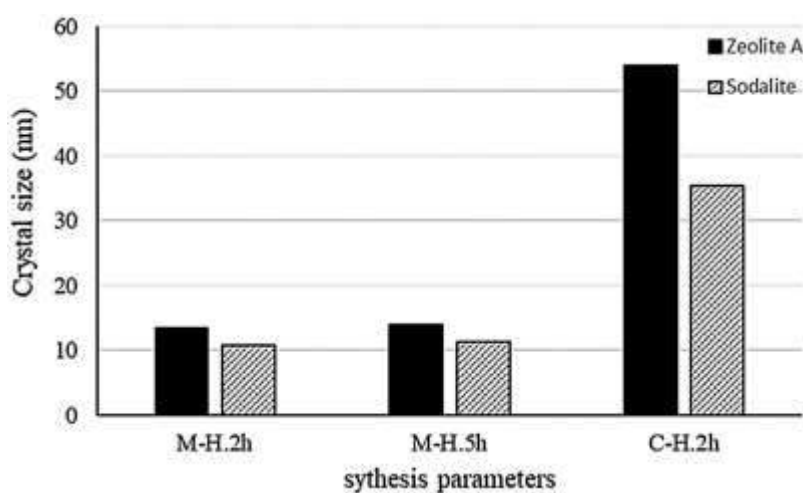


Figure 4: Crystal size of zeolite A and hydroxy-sodalite

FTIR analysis was conducted to identify the functional group on the synthetic zeolite. The data were analyzed based on the Nicodom FTIR Spectra Libraries. These data were obtained from references, such as the general FTIR vibrational region  $300\text{--}400\text{ cm}^{-1}$  (vibrations of the external opening of the pores caused by breathing motion of the ring hole 12),  $420\text{--}500\text{ cm}^{-1}$  (Si-O/Al-O bending vibrations),  $500\text{--}650\text{ cm}^{-1}$  (double ring D4R/ D6R external vibration) which showed the formation of zeolite A,  $650\text{--}850\text{ cm}^{-1}$  (symmetric stretching vibrations of O-Si-O or O-Al-O),  $900\text{--}1250\text{ cm}^{-1}$  (asymmetric stretching vibrations of O-Si-O or O-Al-O),  $1600\text{--}1700\text{ cm}^{-1}$  (O-H bending vibration) which showed the presence of zeolitic water ( $\text{H}_2\text{O}$ ), and  $3400\text{--}3700\text{ cm}^{-1}$  (O-H stretching vibration of Si-OH) [21]. The FTIR spectra of zeolite synthesis which resulted at 3 variations was shown in Figs. 5, 6, and 7.

There were wavenumber  $555.5\text{ cm}^{-1}$  and  $563.21\text{ cm}^{-1}$  for 40 and 60 mins of 2 h ageing using the M-H method. The existence of absorption band in the region around  $500\text{--}650\text{ cm}^{-1}$  showed the double ring D4R or D6R. It was observed that zeolite A was only formed in variation for 40 and 60 mins of 2 h ageing using the M-H method. There was only wavenumber  $563.21\text{ cm}^{-1}$  for 60 mins of 5 h ageing with M-H. It was also found that zeolite A was only formed in variation for 60 mins of 5 h ageing with M-H. There were wavenumbers of  $555.5\text{ cm}^{-1}$  and  $555.5\text{ cm}^{-1}$  for 3 h and 4 h of the 2 h ageing with C-H. The FTIR analysis was matched with the XRD test, that zeolite A was only formed in variation 3 h and 4 h of the 2 h ageing with C-H.

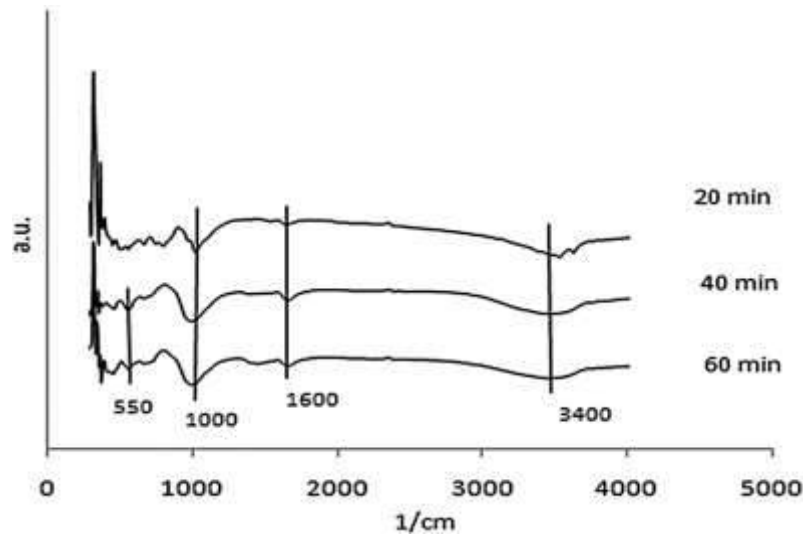


Figure 5: FTIR spectra of zeolite produced from microwave-hydrothermal synthesis for 2 h ageing

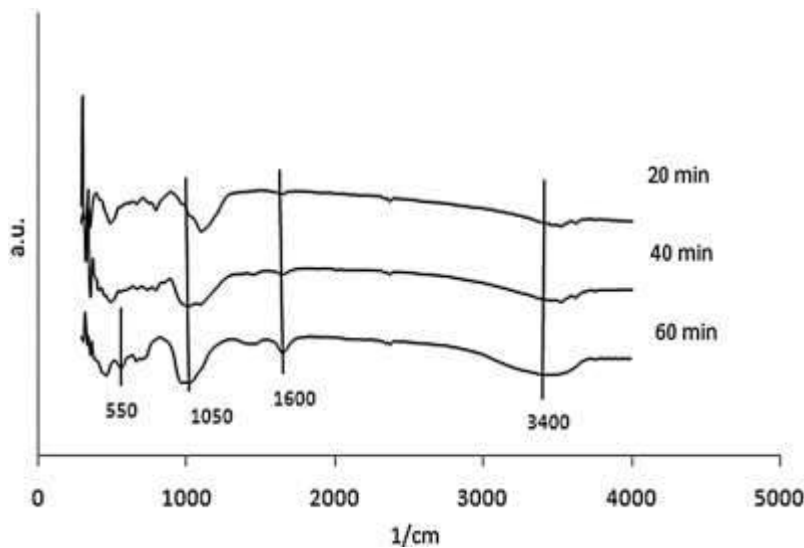


Figure 6: FTIR spectra of zeolite produced from microwave-hydrothermal synthesis for 5 h ageing

Scanning electron micrograph of the M-H process for 2 h ageing with holding time of 20, 40, and 60 mins were shown in Figs. 8a, 8b, and 8c, respectively. It was shown that on variation 20 mins, the formation of grain was not regular, while amorphous and zeolite A has not been formed yet. However, on variation 40 and 60 mins, zeolite A and sodalite were formed. Zeolite A has cubic while sodalite has spherical form with an array of long fibers that surrounded it. The same with M-H for the ageing of 2 h and 5 h and the holding time of 20 mins. The zeolite A formed, as shown in Fig. 6d. that the formation of grain was not regular or amorphous. The spherical form appeared on variation of 40 mins (Fig. 6e), and showed that amorphous silica transformed into a crystal of zeolite. On variation of 60 mins (Fig. 6f), the image showed the formation of many cubes, in the form of zeolite A and sodalite, has spherical form with an array of long fibers that surround it. The grain size of zeolite A and sodalite we're approximately 1  $\mu\text{m}$ .

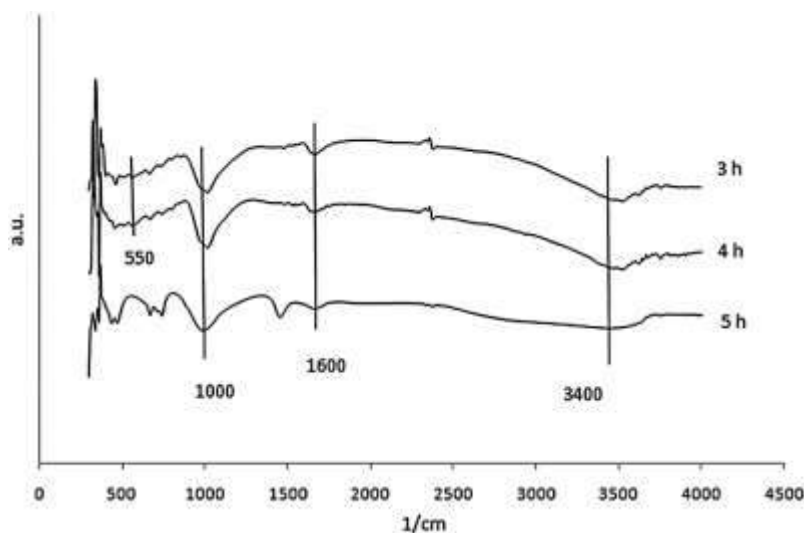


Figure 7: FTIR spectra of zeolite produced from conventional-hydrothermal synthesis for 2 h ageing

The result of the SEM on the variation of 2 h ageing with C-H was shown in Fig. 9. On variation 3 h, the formation of zeolite A and sodalite with a grain size of about 5  $\mu\text{m}$  and 10  $\mu\text{m}$ , respectively were observed (Figs. 9a and 9b). Fig. 9a showed that there was a cubic formation of zeolite A. Fig. 9b showed sodalite phase. While Fig. 9c indicated that the formation of zeolite A and sodalite was not clear on variation 4 h, and only sodalite phase was observed, because zeolite A has been transformed into sodalite (Fig. 9d). The M-H produced smaller and more homogeneous grain size of zeolite A and sodalite, due to faster and homogeneous heating compared to C-H. The formation of sodalite as a side product in the synthesis of NaA was explained by the inadequate mixing. The prolonged heating resulted in the dissolution and regrowth of crystals composition, e.g., when a NaA mixture moved into a HS range, eventually, all NaA were transformed into sodalite. However, when the synthesis mixture stayed in the NaA region, the only sodalite that nucleated was in the inhomogeneous pockets [33].

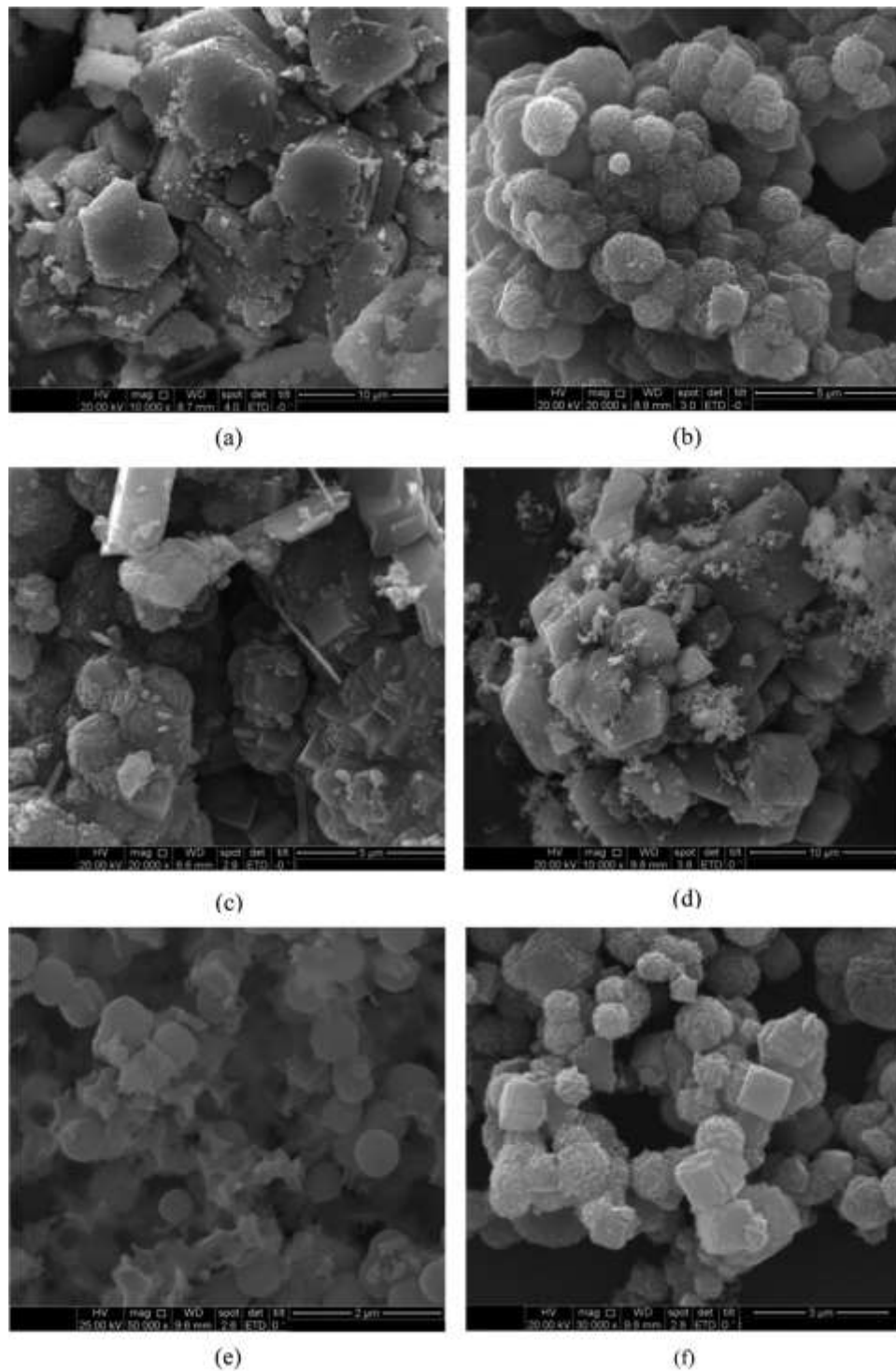


Figure 8: SEM image of synthetic zeolite for 2 h ageing with M-H (a) 20 min (b) 40 min (c) 60 min and 5 h (d) 20 min (e) 40 min (f) 60 min

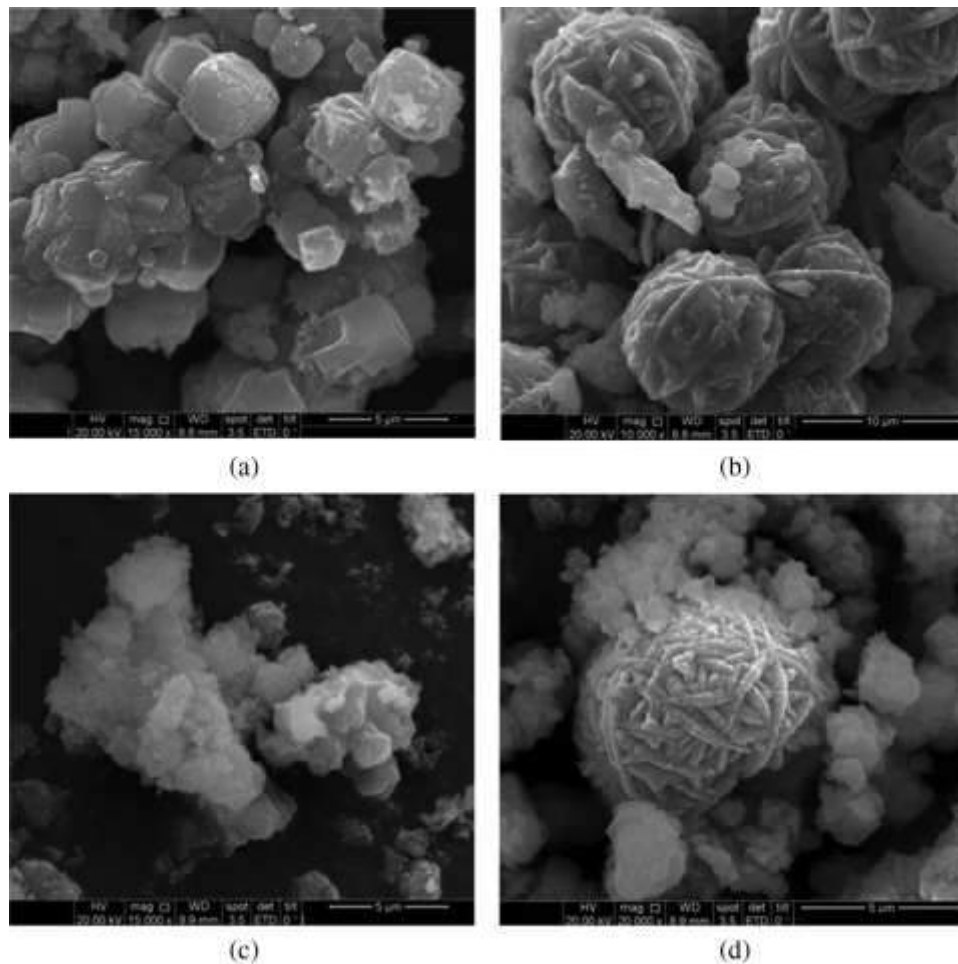


Figure 9: SEM image of synthetic zeolite 2 h ageing with C-H (a) 3 h zeolite A (b) 3 h sodalite (c) 4 h (d) 5 h

#### 4 Conclusions

Zeolite A was successfully synthesized from geothermal waste by conventional-hydrothermal (C-H) and microwave-hydrothermal (M-H) methods. This waste consists of 80.04%  $\text{SiO}_2$  and 0.142%  $\text{Al}_2\text{O}_3$ , while its silica content has high potential as an alternative source for synthesizing zeolite A. The rise of M-H and C-H time increased and decreased the crystallinity of zeolite A and sodalite, respectively. The fast crystallization observed using the M-H method affected the significant reduction in duration to 3 or 4 times shorter, producing smaller and more homogeneous crystal size compared to the C-H method.

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**Conflicts of Interest:** The authors declare no conflicts of interest regarding this study.

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Thu 24/12/2020 13:36

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Dear Sulardjaka Sulardjaka, Sri Nugroho, Norman Iskandar, Agus Purnomo Adi, Deni Fajar Fitriyana,

We are pleased to inform you that the following paper has been officially

accepted for publication:

"Zeolite A Prepared from Geothermal Waste by Microwave-Hydrothermal and Conventional-Hydrothermal".

ID: 11784

Further process will be applied, you will be contacted shortly.

Thank you very much.

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