



Synthesis of Zeolite A from Bituminous Fly Ash by Microwave-Assisted Hydrothermal Method

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Abstract

Zeolite A was synthesized by microwave-assisted hydrothermal method from bituminous fly ash (BFA). BFA is a solid residue from a coal power plant containing high silica and alumina, which are the essential constituents for the formation of zeolite. The ash was pretreated under a hydrothermal process at temperatures of 50°C and 70°C for 12 and 24 hours using 3 M NaOH solution to dissolve Si⁴⁺ and Al³⁺ species from the ash. The results showed that soluble silica was present in the filtrate at 78 wt.% with the Si/Al molar ratio of 64.17 when the ash was pretreated at the temperature of 70°C for 24 hours. After pretreatment, the NaOH-NaAlO₂ solution was added to the filtrate to adjust the Si/Al molar ratio between 0.8 and 2.3 and heated in a microwave at the temperature between 75°C and 105°C for 1 hour. The XRD technique revealed that Zeolite A was formed at the Si/Al molar ratio of 0.8 and under microwave heating between 95°C and 105°C for 1 hour. The QXRD confirmed that 100% of Zeolite A was obtained from microwave heating either at the temperature of 95°C and 105°C. A sharp cutting angle of each cubic crystal was observed from the SEM micrograph.

Keywords: Bituminous Fly ash, Zeolite A, Microwave heating, Si/Al molar ratio, Hydrothermal pretreatment

1. Introduction

Bituminous fly ash (BFA) is a by-product of the combustion of a coal-fired power plant. Each year, the amounts of BFA produced in Thailand are approximately 25 million tons, and there is a tendency to increase rapidly (Buranasing, N., 2017). The most common practice for disposal of these ashes is to place them in a landfill. However, this practice does not economically use the resources and can harm the environment if the landfill is not properly designed. To minimize the ashes going to the landfill, these solid residues should be reused or recycled; for example, partially replacing ordinary Portland cement in construction materials, reusing as a soil amendment in agricultural land, or converting the silica and alumina that are the main components of the ashes into Zeolite. The incorporating of the circular economy principles through the recycling of these ashes leads to the achievement of sustainable development.

Zeolites are crystalline aluminosilicate materials with a three-dimensional tetrahedral framework containing silicon, aluminum, and oxygen. Zeolites are useful in many applications including as adsorbent for treatment of drinking water or wastewater, as ion exchanger in detergents, as catalysts in industrial processes, and as oil refining in the petroleum industry (Moshoeshoe, Nadiye-Tabbiruka & Obuseng, 2017). Many zeolites are, therefore, interested by several researchers to synthesize for specific uses. The hydrothermal process has been widely used amongst others in the synthesis of zeolites but a long reaction time typically up to 48 hours made this technique unattractive. The microwave-assisted hydrothermal method could overcome this disadvantage through a reduced reaction time and energy for the formation of zeolites (Qiu et al., 2018; Kim & Lee, 2009). The use of the microwave-assisted method for the synthesis of Zeolite A at the temperature between 100-110°C for 10-120 minutes was reported (Tanaka et al., 2008; Ansari et al., 2014; Kim & Lee, 2009).

This study aimed to synthesize Zeolite A from bituminous fly ash using hydrothermal pretreatment, followed by microwave heating. The BFA was hydrothermally pretreated under alkali solution at



temperatures of 50°C and 70°C for 12 and 24 hours. The concentration of the soluble silica and alumina (Si^{4+} and Al^{3+} ions) in the hydrothermally pretreated filtrate that was dissociated from the BFA was determined using AAS. The initial Si/Al molar ratio of the treated filtrate was adjusted with the NaOH- NaAlO_2 solution to give the designated Si/Al molar ratio between 0.8 and 2.3 prior to microwave heating. Zeolite A synthesis was conducted in the microwave at a temperature between 75- 105°C for 1 hour. The qualitative and quantitative analyses of Zeolite A were investigated via XRD, QXRD, and SEM techniques.

2. Objectives

- 1) To study the synthesis of zeolite from bituminous fly ash using microwave-assisted hydrothermal method.
- 2) To characterize the zeolite synthesized from bituminous fly ash using QXRD and SEM techniques.

3. Materials and Method

3.1 Materials and Chemicals

Bituminous fly ash used in this study was obtained from BLCP Power Company, Rayong, Thailand. The ash was collected from the electrostatic precipitators. Sodium Hydroxide Micropearls (FORMOSODA-P, 99 wt%), Sodium Aluminate (Sigma-Aldrich), deionized water, and filter paper GF/C dia. 47 mm (Whatman) were used in this work.

3.2 Synthesis

20 g of BFA and 500 ml of 3 M NaOH solution were mixed in a hydrothermal reactor. The slurry was stirred using a magnetic stirrer and heated at 50°C and 70°C for 12 and 24 hours. The solid was then separated from the mixture by a filtration process, and the volume of the filtrate obtained was about 450 ml. The Si/Al molar ratio of the filtrate was varied between 0.8-2.3 (Hollman, Steenbruggen & Janssen-Jurkovicova, 1999) using the NaOH- NaAlO_2 solution. The solution of NaOH- NaAlO_2 was prepared by dissolving the calculated amount of NaAlO_2 into 100 ml of 3M NaOH solution before mixing with 300 ml filtrate, stirred at room temperature for 5 minutes. The mixture of the solution was subjected to microwave heating at 75-105°C for 1 hour. After the microwave treatment, the solid was separated by filtration, washed with deionized water until a pH of 10 was maintained to remove excess Na ions (Iqbal et al. 2019), and oven-dried at 100 °C for 12 hours before the XRD analysis.

3.3 Characterization

The chemical composition of the ash was determined by an X-ray fluorescence (XRF) spectrometer (Bruker D8 Discover). The products obtained from the microwave synthesis were identified for the mineral phases, especially Zeolite A using the X-ray diffraction (XRD) technique (Bruker D2 phaser powder diffractometer). The quantitative X-ray diffraction (QXRD) technique was used to calculate the amounts of zeolite formation and was carried out using the software named TOPAS. The morphology of the zeolite was assessed using the Scanning Electron Microscope (SEM; JEOL, JSM7800F). Concentrations of Si^{4+} and Al^{3+} in the filtrate obtained from hydrothermal pretreatment were analyzed by atomic absorption spectroscopy (AAS; Shimadzu, AA-7000). The surface area and pore size distribution were determined based on Braunauer-Emmett-Teller's (BET; Micromeritics, 3Flex) multilayer adsorption theory.

4. Results and Discussion

4.1 Characterization of BFA

The chemical composition of BFA determined by the XRF technique is shown in Table 1. The results showed that the two main oxides of fly ash; SiO_2 and Al_2O_3 , were present at 53.6 and 25.4 wt% with the presence of CaO and Fe_2O_3 of less than 10 wt%. The initial Si/Al molar ratio of the BFA was obtained by a calculation and equals 1.8. According to the XRD pattern, the crystalline phases of SiO_2 were present in the



form of quartz and tridymite, those of Al_2O_3 were present in the form of aluminum oxide, whereas the aluminosiliceous phases present in the BFA were in the form of mullite (Figure 1).

Table 1 Chemical composition of bituminous fly ash (wt.%)

	%
SiO_2	53.6
Al_2O_3	25.4
CaO	8.25
Fe_2O_3	5.89
TiO_2	1.63
K_2O	1.56
MgO	0.984
P_2O_5	0.967
SO_3	0.644
Na_2O	0.495
SrO	0.197
ZrO ₂	0.071
MnO	0.059
Other	0.253
Si/Al molar ratio	1.8

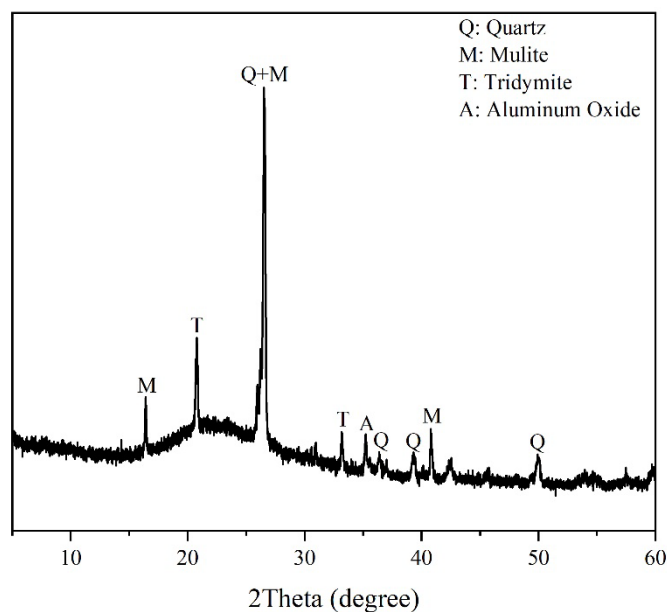


Figure 1. The XRD pattern of the as-received BFA



4.2 Effect of hydrothermal pretreatment of BFA

The concentrations of Si^{4+} and Al^{3+} species in the filtrate after the hydrothermal pretreatment with 3 M NaOH solution at temperatures of 50°C and 70 °C for 12 and 24 hours are present in Figure 2. The solubility of silica from the BFA in alkali solution depends on temperature and time. The experimental results showed that the concentrations of Si^{4+} in the filtrate after pretreatment at 50°C for 12 and 24 hours were 82,500 and 106,770 ppm (mg/kg), respectively, and at 70°C for 12 and 24 hours were 131,666 and 153,958 ppm (mg/kg), respectively. The presence of SiO_2 in the BFA used in this work was in the form of quartz and tridymite. The glassy phase of SiO_2 requires higher energy to dissolve into Si^{4+} ions compared with the amorphous phase, which is the reason why the concentrations of Si^{4+} ions present in the filtrate after hydrothermal pretreatment at 70°C was obtained at all reaction time observed. A significantly lower concentration of Al^{3+} ions was obtained compared with Si^{4+} ions at all experimental conditions performed. It could have arisen from the initial amount of SiO_2 (53.6%) in the BFA that was doubled of Al_2O_3 (25.4%). Another explanation could be because the solubility of SiO_2 and Al_2O_3 is different. Al_2O_3 is reported to have an increased solubility at pH lower than 3 or greater than 9 (Adhikari, S., 2008). It could be possible that the Al^{3+} ions can react with the readily soluble Si^{4+} ions in the alkali solution during hydrothermal pretreatment, and thus, leading to the formation of aluminosilicate gel. As a result, a low concentration of Al^{3+} ions in the filtrate was low.

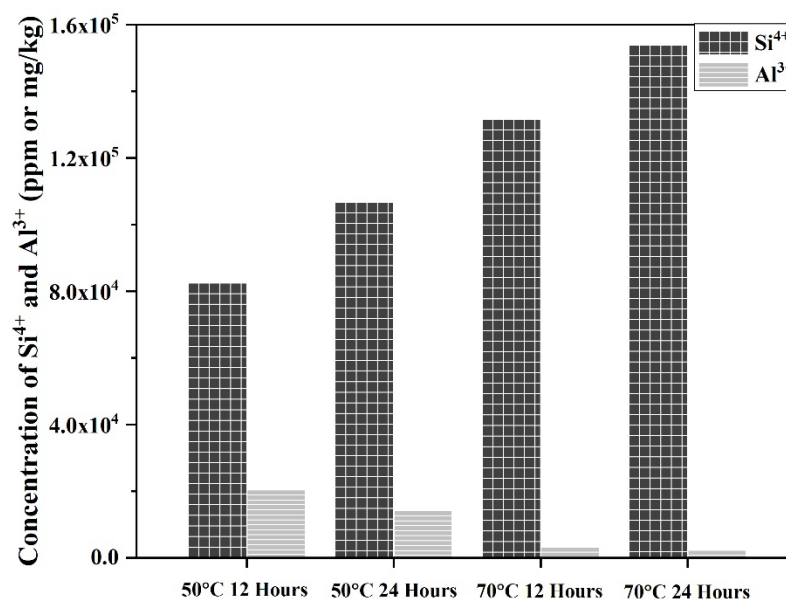


Figure 2. The concentration of Si^{4+} and Al^{3+} ions pretreated in 3 M NaOH solution at 50°C and 70°C for 12 and 24 hours

Figures 3a and 3b show the XRD patterns of BFA residue after hydrothermal pretreatment with 3 M NaOH at 50°C and 70°C for 24 hours. After the pretreatment at 50°C (Figure 3a), the appearance of the peaks for garronite and thermonatrite was observed while the peaks of tridymite and aluminum oxide present in the as-received BFA were disappeared. Garronite is a crystalline form of zeolite whereas thermonatrite is a crystalline aluminosilicate product. When the BFA was pretreated at 70°C, similar diffractograms to that pretreated at 50°C were observed, except that the formation of hydroxy sodalite was found (Figure 3b). The formation of various crystalline phases of aluminosilicate products during the hydrothermal pretreatment at 70°C resulted in a decrease of the intensity of the peaks for quartz and mullite when compared with the pretreatment at 50°C. The XRD results are in good agreement with the variation in the concentration of Si^{4+} and Al^{3+} ions in the filtrate of hydrothermal pretreatment (Figure 2).

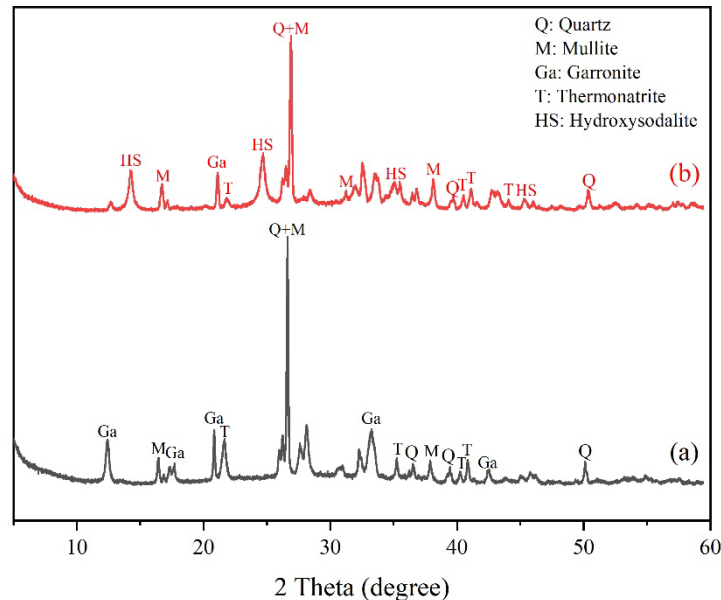


Figure 3. The XRD patterns of the BFA pretreated in 3 M NaOH solution at 50°C (a) and 70°C (b) for 24 hours

4.3 Synthesis of Zeolite A

The filtrate after hydrothermally pretreated at 70°C for 24 hours was selected for further synthesis of Zeolite A. The initial Si/Al molar ratio in the selected filtrate was 64.17 and adjusted to between 0.8 and 2.3 with the NaOH- NaAlO₂ solution. The filtrates with designated Si/Al molar ratio were subjected to microwave heating at 75°C for 1 hour, and the XRD patterns were presented in Figure 4. No crystalline phases were formed except at the Si/Al molar ratio of 0.8 with the appearance of several low-intensity peaks detected. The hydrothermally pretreated filtrate with the Si/Al molar ratio of 0.8 was, therefore, selected for further study.

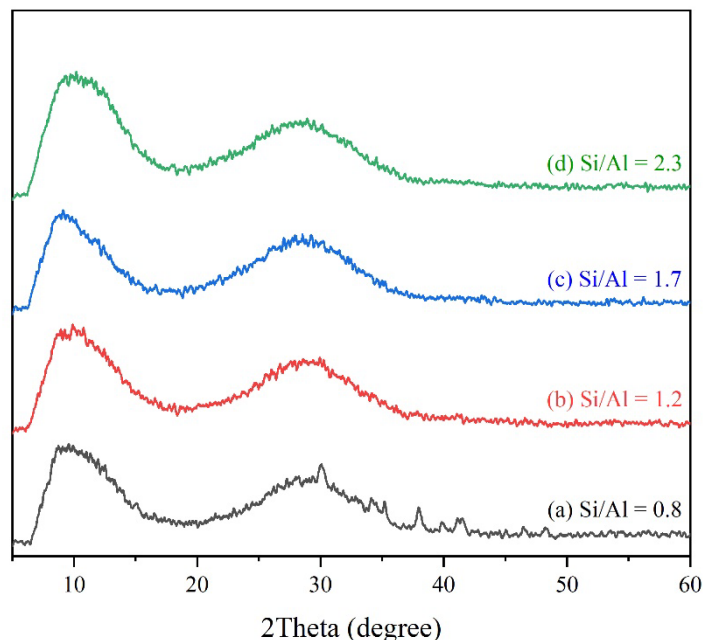


Figure 4. The XRD patterns of the hydrothermally pretreated filtrate at different Si/Al molar ratio and microwave heating at 75°C for 1 hour

The XRD patterns of the hydrothermally pretreated filtrate at the Si/Al molar ratio of 0.8 and microwave heating at 95°C and 105°C for 1 hour are shown in Figures 5a and 5b. The XRD diffractograms from both synthesis conditions showed sharp peaks of crystalline phases of Zeolite A (PDF 04-023-0607). Although the intensity of the main peaks obtained from the XRD analysis of zeolite synthesis at 105°C was slightly higher than that at 95°C, the QXRD results confirmed the presence of Zeolite A at 100% from both conditions. The morphological analysis of Zeolite A revealed the presence of the cubic crystals (Figures 6a and 6b). The SEM micrographs showed that Zeolite A formation at 105°C (Figure 6b) having more cubic crystals with a sharp cutting-edge when compared with that at 95°C, which indicates that a better crystallization of Zeolite A was obtained. Besides, the size of the cubic crystals was observed to be shifted to smaller size crystallines. The surface area of Zeolite A synthesized using microwave heating at temperatures of 95°C and 105°C were 2.370 and 3.170 m²/g, with the average particle size at 95°C and 105°C of 2,531 and 1,892 nm, respectively (Table 2). The experimental results are in good agreement with the SEM micrographs.

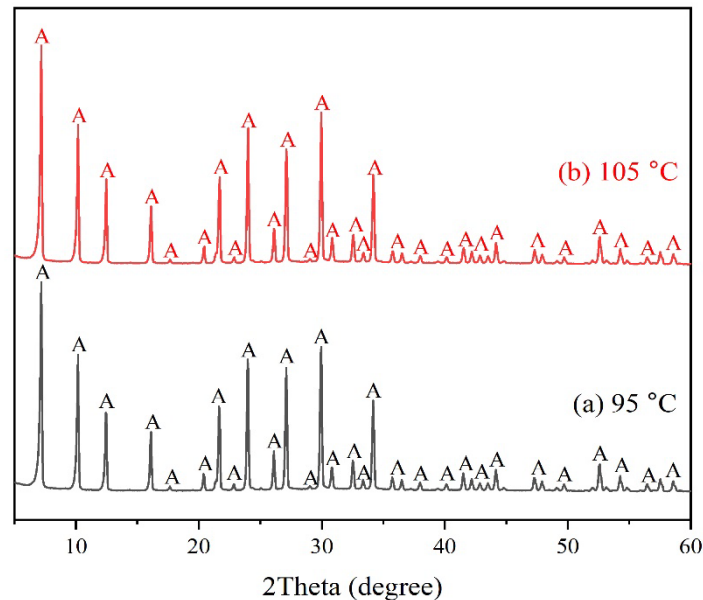


Figure 5. The XRD patterns of the hydrothermally pretreated filtrate at the Si/Al molar ratio of 0.8 and microwave heating at 95°C (a) and 105°C (b) for 1 hour; where A = Zeolite A

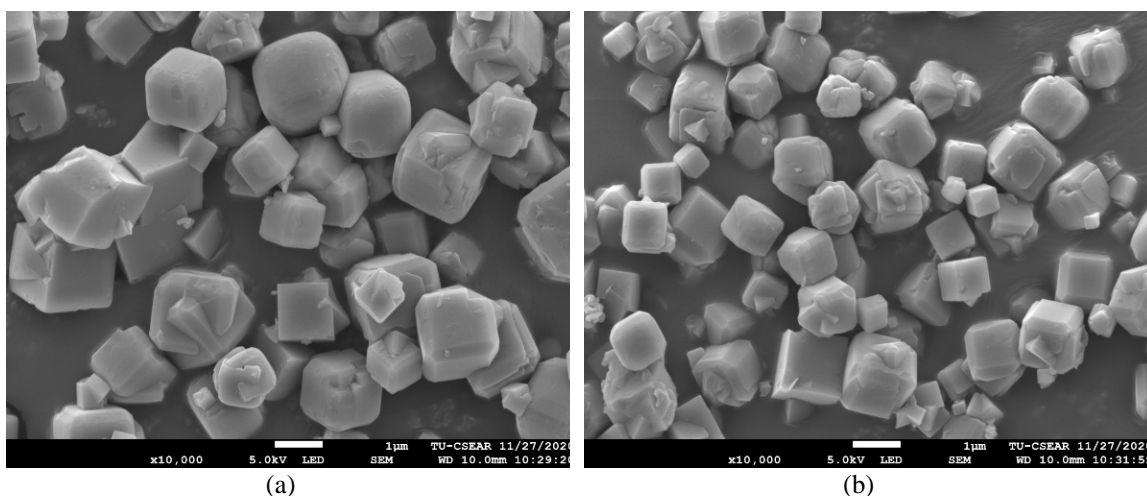


Figure 6. The SEM photographs of Zeolite A synthesized from hydrothermally treated filtrate at the Si/Al molar ratio of 0.8 and microwave heating at different temperatures for 1 hour; 95°C (a) and 105°C (b)

Table 2 Surface area and average particle size of Zeolite A

Temperature (°C)	Surface Area (m ² /g)	Average particle size (nm)
95	2.370	2,531
105	3.170	1,892

5. Conclusion

This work demonstrated that the bituminous fly ash (BFA), a solid residue from the coal power plant, can be reused as starting material for the synthesis of Zeolite A. The QXRD results showed that 100% of



Zeolite A crystalline could be obtained using a microwave-assisted hydrothermal process. The experimental results suggested that the hydrothermal pretreatment of BFA at 70°C for 24 hours and adjusted the Si/Al molar ratio of the filtrate to 0.8, followed by microwave heating at 95°C and 105°C for 1 hour, is favored for the formation of Zeolite A. Further study is necessary to identify the properties of the obtained zeolite such as cation exchange capacity (CEC), surface area, and pore size distribution.

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