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Synthesis of Na-A zeolite from water treatment residue using hydrothermal and microwave techniques

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Abstract. Na-A zeolite was synthesized from water treatment residue (WTR) using hydrothermal and microwave techniques. WTR was brought from Metropolitan Waterworks Authority (Thailand) and was activated by firing at 700 °C for 3 h in an electric furnace. The activated WTR was reacted with 3 M NaOH solution in a reactor under a controlled temperature of 80, 90 and 100 °C for 8, 10, 12, and 14 h. SEM (Scanning electron microscopy) images reveal the cubic crystal of zeolite. The highest cation exchange capacity (CEC) was obtained from sample synthesized at 90 °C for 14 h and gave the CEC value of 3.14 meq/g Ca²⁺. For the microwave technique, the raw materials were reacted at 80 90 and 100°C for 30, 60, and 120 min. Results showed that the sample obtained at 80 °C for 30 min represented the highest CEC value of 0.29 meq/g Ca²⁺.

1. Introduction

The waste from water treatment is a water treatment residue by coagulants and other chemical reagents in the purification process. The number of residue from the process about 100 ton/day and removal of WTR has carried out lead drilling for as much as 11 million baht a year [1]. The Metropolitan Waterworks Authority (Thailand) has studied to develop WTR in agriculture and industry. The main chemical components of WTR are silica, alumina, ferric oxide and lime. The substances of zeolite are almost of silica and alumina and these residues are high of silica and alumina ratio of 1-2 [2] the raw material is appropriate for zeolite synthesis. The synthesis of zeolite Na-A (Na₁₂ [(AlO₂)₁₂(SiO₂)₁₂].27H₂O) is a porous aluminosilicate compound with numerous excellent properties, such as non-toxicity, high porosity, good thermal stability, high Ca²⁺ exchange capacity, and functional molecular sieve [3] which is generally synthesized as hydrothermal synthesis can be effected under temperatures and pressures below the critical point [4] and Microwave technique has a short time to crystallization and homogeneous nucleation [5]. The objective of the study was to compare the properties of Na-A zeolite by the hydrothermal technique with microwave heating.

2. Material and methods

2.1. Raw material and chemicals

The raw WTR samples were collected from the Metropolitan Waterworks Authority (Thailand). The composed of WTR Si/Al molar ratio is around 1.78. Sodium Hydroxide (3M NaOH) as alkali



hydroxide is the used material for the preparation of Na-A zeolite. The solution for cation exchange capacity (CEC) tests using complexometric titration with EDTA.

2.2. Experimental

2.2.1. Synthesis of Na-A zeolite. WTR was crushed into different particle size and calcination at 700 °C for 3 h. The sample with the particle size larger than 325 mesh sieve hole was used to synthesize. For hydrothermal synthesis WTR obtained undergo alkaline treatment by mixing 160 g of WTR with 800 ml of 3M NaOH at 80, 90, and 100 °C for 8, 10, 12, and 14 h under stirring at 500 rpm. In the microwave synthesis at 1000 W the raw materials were reacted at 80 90 and 100°C for 30, 60, and 120 min. At the end of synthesis, the reaction mixtures were filtered and washed with distilled water until the pH of the filtrate is below 9. Then the samples were oven dried overnight at 105 °C.

2.2.2. Sample characteristics. The Na-A were characterized using different analytical techniques. The morphology of Na-A was studied using Scanning Electron Microscopy (SEM). The chemical characterization was performed by the X-ray fluorescence (XRF) and Cation exchange capacity (CEC).

3. Results and Discussion

3.1 The chemical characterization of WTR

The chemical compositions of the WTR analysis data from XRF show that in Table 1. The mainly composed of WTR is SiO₂ 54.200 wt% and Al₂O₃ 30.400 wt%. The Si/Al molar ratio is around 1.78. The components of WTR can be used in the synthesis of zeolites, which is quite close to the Si/Al ratio 1-2 in Na-A [2]

Table1. Chemical compositions of WTR powder

Ingredients	Composition (wt.%)
SiO ₂	54.200
Al ₂ O ₃	30.400
Fe ₂ O ₃	8.500
K ₂ O	2.300
MgO	1.030
TiO ₂	0.885
CaO	0.759
SO ₃	0.538
P ₂ O ₅	0.527
Na ₂ O	0.254
LOI	0.33

3.2 Characterization of zeolite Na-A

3.2.1. Cation exchange capacity. The cation exchange capacity of all synthetic products was evaluated and expressed in CaCO_3 (meq/g) anhydrous zeolite Na-A from the solution having the hardness of CaCO_3 . The highest cation exchange capacity in the hydrothermal process shows that in Table 2 is about 3.14 meq/g obtained in To explore the effect of crystallization on the temperature rose from 80 to 100 °C zeolite Na-A could not be obtained until the temperature was below than 90 °C. When the temperature was above 90 °C CEC value are decreasing steadily [6].

Table2. Cation exchange capacity of Na-A zeolite by hydrothermal process

Time (h)	CEC (meq/g)		
	80°C	90°C	100°C
8	0.28	1.46	1.38
10	0.30	2.47	1.54
12	0.37	2.97	0.99
14	0.38	3.14	0.60

The sample synthesized from WTR at 90 °C for 14 h. The synthetic products obtained by microwave exhibited in Table 3 the maximum CEC at 80 °C for 30 min. When the crystallization time was the longer reaction the poorly developed Na-A would be obtained, thus the crystallization time of 30 min should be maintained to improve the crystallinity and avoid phase transformation [7].

Table3. Cation exchange capacity of Na-A zeolite by the microwave process

Time (min)	CEC (meq/g)		
	80°C	90°C	100°C
30	0.29	0.13	0.13
60	0.19	0.12	0.12
120	0.12	0.11	0.10

3.2.2. Scanning electron microscope. The size and shape of crystals of minerals can be verified by SEM micrographs of the raw materials and the end product obtained from the zeolite process. The SEM micrographs of the WTR reveal the presence of among of amorphous in Fig. 1A. The morphology and particle size of the optimum samples are shown in Fig. 1B and 1C. The SEM micrographs for the best hydrothermal synthesis zeolite Na-A at 90 °C for 14 h showed the formation of zeolite Na-A crystal of cubic shape (Fig. 1B). From the micrographs of the best microwave synthesis at 80 °C for 30 min it is possible to see the presence of zeolite Na-A crystal of cubic shape with a rounded edge. Thus, the synthesis time of crystallization by microwave synthesis was shorter than hydrothermal synthesis. Moreover, zeolite Na-A synthesized by hydrothermal is composed of well-shaped cubic crystals, while Na-A under pulsing microwave consists of sphere grains without well- developed crystal faces [8].

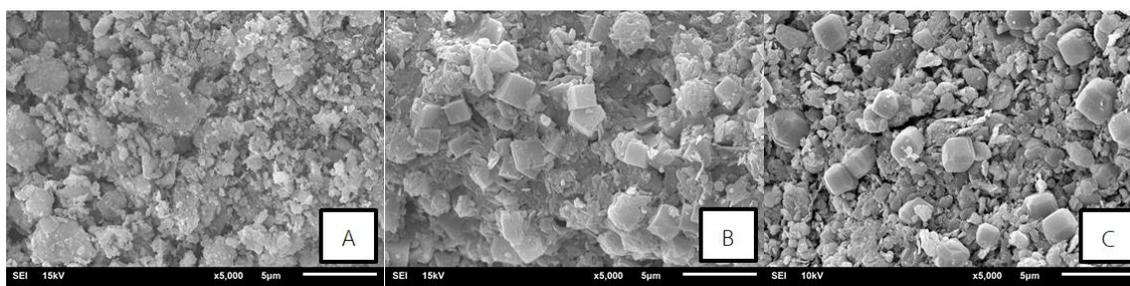


Figure 1. SEM micrographs of (A) WTR, (B) synthesis Na-A prepared by hydrothermal, (C) microwave.

4. Conclusions

The synthesis of zeolite Na-A from water treatment residue was done by the hydrothermal and microwave technique of synthesis. The hydrothermal synthesis gave cubic crystal of zeolite Na-A having optimum CEC at 90 °C for 14 h. Whereas, the microwave synthesis yielded cubic crystal of zeolite with cubic shape with rounded edge and CEC high-value capacity at 80 °C for 30 min. Hence, the crystallization time by microwave was shorter than hydrothermal synthesis, while zeolite Na-A synthesized by hydrothermal is composed of well-shaped cubic crystals. Therefore, hydrothermal synthesis also has the advantage of the operating alkaline process variables to achieve higher yield, purity, cation exchange capacity and crystallinity. The hydrothermal method can obtain the high temperature and high pressure in a closed reaction systems, it takes a long time to complete the reaction. Nevertheless, the microwave irradiation as energy sources could lead to homogenous nucleation and uniform distribution of heat leading to a decrease in the reaction time from days down to hours and even minutes. The disadvantages of microwave irradiation are from its limitations and preparation.

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