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Characterization and Activation of Indonesian Natural Zeolite from Southwest Aceh District-Aceh Province

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Abstract. This study aims to identify the effect of activation processes of Indonesian zeolite from Southwest Aceh District, Aceh Province on the physical characteristics and chemical contents changes. The work was conducted by downsizing of natural zeolite into nano particle size, treating it physically (heated up to 105˚C) and chemically (soaked with 0.5 M HCl for 1 hour), and finally calcining it at the temperature of 350° C for 2 hours. The natural and activated nano zeolites were then characterized by using SEM, BET, XRD, XRF and FTIR in order to examine their characters and chemical contents. The characterization results showed that the activated nano zeolite has better appearances than the natural one. The XRD analysis showed that the main minerals of zeolite are quartz and calcite clinochlore. Further, the XRF analysis showed that there are elements of magnesium, calcium and potassium which can be as a cation exchange with other metal elements. Based on the identified properties, this zeolite showed a good performance to be used as an adsorbent in waste water treatment process, especially after activated.

1. Introduction

Zeolite is a natural material that can be utilized in various applications including as adsorption, catalyst, building industry, agriculture, soil remediation and energy (Wang and Peng, 2010). Zeolite was first discovered in 1795 by A F Cronstedt, a mineralogist from Sweden. Based on his research, zeolite can release water rapidly when heated so it looks like a stone boiling. Zeolite name comes from the Greek "zeo" which means to boil and "lithos" means stone (Izci and Izci, 2007).

Zeolite contained in tufa rocks are formed from the sedimentation of volcanic ash that has been experiencing a process of alteration. Alteration process took place on a new depositional environment causing materials change from volcanic glass into mineral zeolite. The geology zeolite formed in a different environment, precipitated zeolite derived from volcanic sediment on the lake environment is alkaline and diagenetic alteration of volcanic ash, hydrothermal deep-sea sediments (Ibrahimi and Sayyadi, 2015). In this study the zeolite obtained from the Province of Aceh, Southwest Aceh District. The data from the Department of Mines and Energy of Southwest Aceh District informs that in this area has encountered outcrops zeolite, but the reserve and quality of that mineral zeolite is still unknown. Based on the Tapaktuan geological map sheet from the Geological Research and Development Centre, Bandung 1982, there are several volcano formations; among them is Tapaktuan Volcano Formation. From geological maps and field observations, in several locations of Southwest

Aceh District there are outcrops of the mineral zeolite. Different environmental conditions affect the color of zeolites, which are green, greenish-white, red and white meat, brown bluish gray.

Zeolites are hydrated silicates of alumina compounds with alkali and alkaline earth cations. The structure of natural zeolite formed by alumina silica atoms tetrahedral form three-dimensional structures that are connected with one another through the sharing of oxygen atoms so as to form cavities and channels that contain water molecules and cations alkali and or alkaline (Mirzaei et al., 2016). Zeolite structure, divided into three components, namely the framework of alumina silicates, empty space interconnected containing metal cations and water molecules. The water contained within the zeolite pores can be removed by heating to push the water in the zeolite pores (Lestari, 2010). Natural zeolite is a zeolite obtained directly from nature, has a cheaper price than the zeolite synthesis. Natural zeolites have advantages including that of low cost because of the availability of natural zeolite with an abundance of cation exchange capacity, acts as a molecular sieve, have a high surface area due to the structure of the porous, has structural stability was good although in acidic conditions, capable of neutralizing the acid solution through H^+ ion exchange of cations in the solution with the zeolite.

Based on the fact that there are a number of advantages of natural zeolites attract the interest of researchers in exploiting natural zeolite as an adsorbent to absorb heavy metals. Erdem et al. (2004) used natural zeolite to adsorb the Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+}ions in industrial waste. They found that the natural zeolite types clinoptilolite has a good ability to adsorb these ions; an optimum ions adsorption sequence was $Co^{2+}>Cu^{2+}>Zn^{2+}>Mn^{2+}$. The adsorption of heavy metal ions in the acid mine water by using natural zeolite adsorbent was conducted by Motsi et al. (2009). In that study, natural zeolite applied as an adsorbent without any chemical modification to adsorbs Fe^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} in the acid mine drainage. They observed the effect of zeolite mass, solution pH, competing ions and heat treatment. They concluded that the adsorption of heavy metal ions from solution follows the sequence $Fe^{3+}>Zn^{2+}>Cu^{2+}>Mn^{2+}$. Behind its leading, natural zeolite has also the disadvantage since its content of impurities (alkali and alkaline earth metals) and the water content that can reduce the absorption capacity.

Potential resources of zeolites in Southwest Aceh District, Aceh Province characterization needs to be done to reveal the physical and chemical properties of natural zeolite particles in order to optimize the utilization of zeolite and to improve the performance with the physical and chemical activation to remove impurities contained in the zeolite pores. Improving performance is one of the natural zeolite mineral resource conservation efforts that enhance the value-added minerals. The objectives of this paper were to investigate the influence of activation treatments (both physically and chemically) on the physical characters and chemical contents changes of Indonesian zeolite from Southwest Aceh District.

2. Methodology
The experimental procedure consists of materials and methods, zeolite activation and characterization.

2.1. Materials and methods
Equipment used in this study are jaw crusher, ball mill, sieve shaker, oven dryer (Memmeth DIN 12880-KI), X-Ray Difraction (XRD, Shimadzhu 6000), X-Ray Florence (XRF, Spectroxepos), FTIR (Shimaddzu Prestige 21), stirrer plate (Barnstead Thermolyne Cimarec), furnace, drop pipette, analytical scale (Shimadzu AW-220), measuring pipette 25 mL, measuring cylinder 100 mL, erlenmeyer 250 mL and distilled water bottle. Meanwhile, materials used in this study were natural zeolite from Southwest Aceh District, Hydrochloric acid (HCl) and distilled water.

2.2. Experimental and analytical

2.2.1. Activation of zeolite. Zeolite activation procedure is shown in Figure 1. At first, natural zeolite was cleaned and dried, and then pulverized by using jaw crusher and ball mill. Product of ball mill further screened using sieve shaker until the residue of zeolite particles were obtained in nano size. To remove the impurities, nano zeolite was washed with distilled water for 1 hour at temperature of 70°C, and then precipitated. Next, the sediment formed was dried at temperature of 105°C. After that, it was activated with 0.05 M HCl at the ratio of zeolite to acid by 1:3; the mixture was stirred for 1 hour at

temperature of 70˚C, and re-precipitated. The sediment formed at this step was dried again at 105˚C, then washed with distilled water for 1 hour at temperature of 70˚C and precipitated. Finally, the sediment formed here then dried at temperature of 105˚C and calcined at 350˚C during 2 hours.

Calcination is done in order to evaporate the trapped water in the pores of the zeolite and to burn the organic compounds contained in the zeolite so that the space between the pore becomes relatively clean. This is an effort to make the surface area of zeolite increases that consequently increase the adsorption capacity of the zeolite as well (Utubira et al., 2006).

2.2.2. Characterization of zeolite. The physical characteristics and chemicals contents for both natural and activated nano zeolites were examined by Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET), X-Ray Diffraction (XRD), X-Ray Florence (XRF), and Fourier Transform Infrared (FTIR).
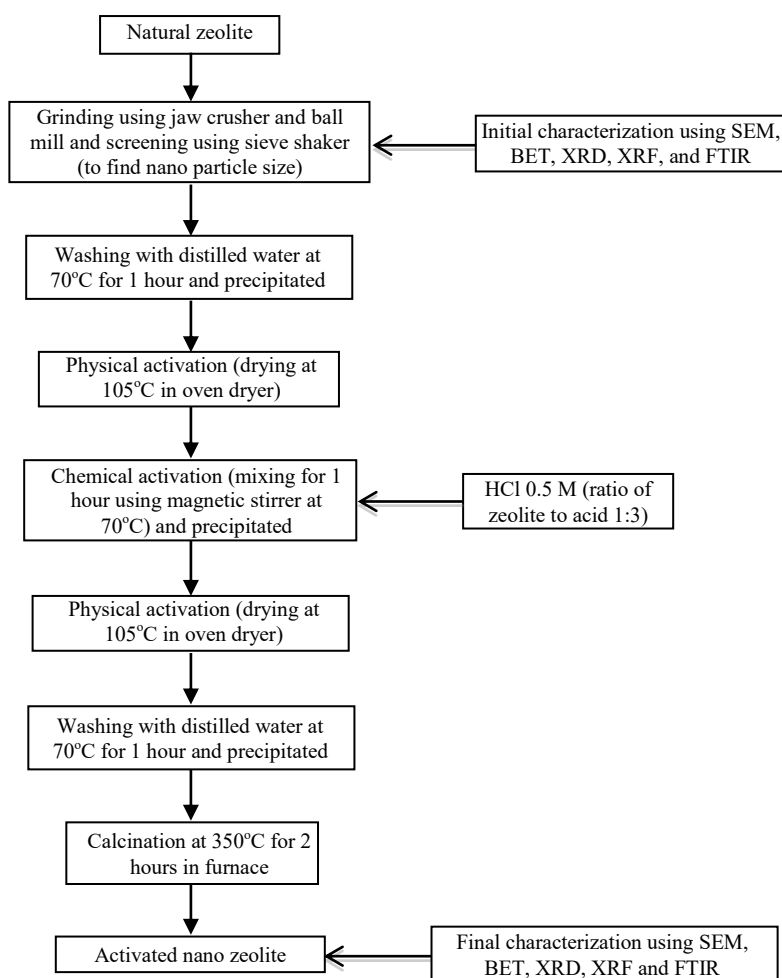

Figure 1. Schematic flow of the process

A scanning electron microscope (SEM) is used to obtain information about the surface topography and composition. The main SEM components include: source of electrons, column down which electrons travel with electromagnetic lenses, electron detector, sample chamber, computer and display to view the images. The zeolite sample is mounted on a stage in the chamber area and both the column and the chamber are evacuated by a combination of pumps. The position of the electron beam on the sample is controlled by scan coils situated above the objective lens. These coils allow the beam to be scanned over the surface of the sample. This beam scanning, as the name of the microscope suggests, enables information about a defined area on the sample to be collected. As a result of the electron-sample interaction, a number of signals are produced. These signals are then detected by appropriate detectors. Further, the specific surface area was measured using SHIBATA APP.SA-1100 at the nitrogen flow rate of 150 ml/min. The APP.SA method is based on the amount of nitrogen adsorbed on

the surface of solid particle. Measurement performed at 77.362 K with sample mass 0.2772 g. Thereafter, the sample of nano zeolite powder put in XRD instrument which connected with the computer to view the data. The XRD analysis is based on constructive interference of monochromatic X-rays and a crystalline sample: The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. The XRD data from the computer analyzed with MATCH software to find the crystal's structure and the composition of mineral.

XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. The sample of nano zeolite powder put in XRF instrument. The sample is irradiated with high energy X-rays from a controlled X-ray tube. When an atom in the sample is struck with an X-ray of sufficient energy (greater than the atom's K or L shell binding energy), an electron from one of the atom's inner orbital shells is dislodged. The atom regains stability, filling the vacancy left in the inner orbital shell with an electron from one of the atom's higher energy orbital shells. The electron drops to the lower energy state by releasing a fluorescent X-ray. The energy of this X-ray is equal to the specific difference in energy between two quantum states of the electron. The measurement of this energy is the basis of XRF analysis.
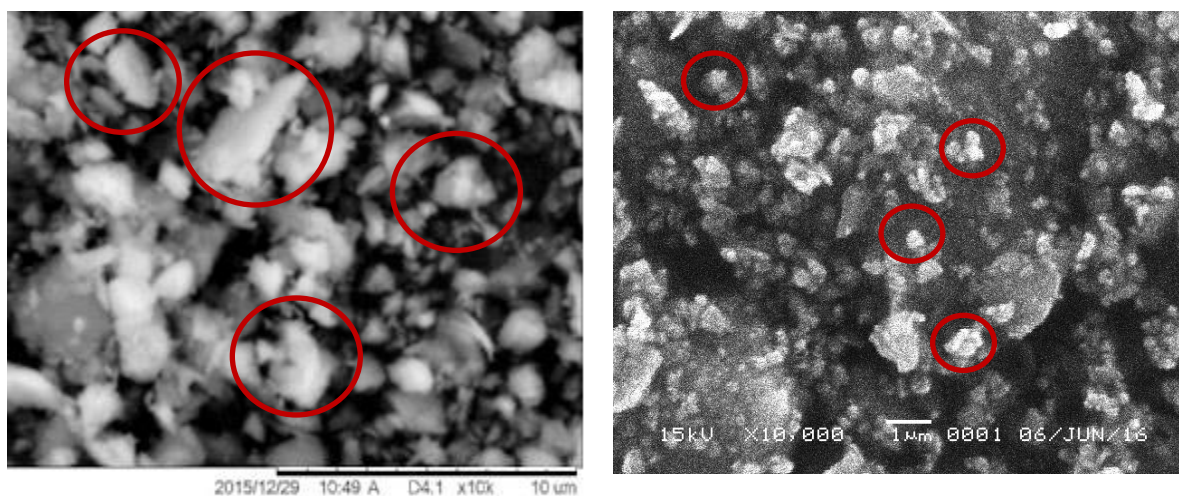
Finally, in order to investigate the properties changes achieved due to activation treatments, the functional groups analysis was attempted by a Fourier Transform Infrared FT-720 spectrometer (FTIR). Samples preparation in the FTIR test was done by the KBr pellets method. The functional groups absorbance of the activated nano zeolites were then compared to natural one and previous data published elsewhere.

3. Results and discussion
The observation results and discussion are out lined in this section. Discussion will be focused on the morphology, surface area and chemical contents for both natural and activated nano zeolites.

3.1. Morphology of zeolite
Characterization by SEM used to determine the morphology of natural and activated nano zeolites. Figure 2a is the SEM images with 10,000X enlargement of the natural nano zeolite.

(a)   SEM image of natural nano zeolite   (b)   SEM image of activated nano zeolite

Figure 2. SEM images of zeolite before and after activated.

Morpholgy of natural zeolite showed a flaky heterogeneous form, as indicated by the circle. Moreover, Figure 2b is the result of SEM image of activated nano zeolite at the same scale enlargement. In opposite, the morphology of nano zeolites after activation presented a grains-like form, as well as has been investigated by Noroozifar et al. (2014) and Mirzaei et al. (2016). They stated that the appearance of the nano zeolite SEM image has a drusy texture, i.e. it looks like a flake crystal with high micro porosity (as highlight by the circle).

3.2. Surface area
Further characterization of zeolite was done by BET to determine the surface area. The results show that the BET surface area of nano-pore of the activated nano zeolite surface area is 12.238 m²/g, pore volume is 0.054 cm³/g and pore size is 177.261 Å or 17.726 nm (Table 1). From the view point of surface area, pore volume and pore size the activated nano zeolite is not quite significant from the natural one. This phenomenon might prove the fact that both natural and activated zeolite was characterized in the nano particle sizes. Those BET data also showed that the nano-pore size of zeolites before and after activation can be classified as a meso-porous size. According to IUPAC, meso-porous diameter lies in the range of 2-50 nm. Nano particle sizes have a higher of ratio of surface area to pore volume compare to similar particles which has larger particle size. This makes the nano-particles more reactive in the adsorption behavior.

Table 1. Data of surface area

	Surface Area (m²/g)	Pore Volume (cm³/g)	Pore Size (Å)
Natural nano zeolite	10.469	0.052	200.300
Activated nano zeolite	12.238	0.054	177.261

3.3. Chemical contents
The result of XRD (Figure 3a) shows that the natural nano zeolite has a composition of mineral quartz (SiO_2), clinochlore [$(Mg, Fe)_6 (Si, Al) 4O_{10} (OH)_8$], calcite ($CaCO_3$), as shown by sharp intensity in the region $2\theta = 26.65°$ (d = 3.34 Å), which is a characteristic of mineral quartz (SiO_2) and reflection with the greatest intensity $2\theta = 29.43°$ (d = 3.03 Å) is a characteristic of mineral calcite ($CaCO_3$), and mineral clinochlore [$(Mg, Fe)_6 (Si, Al) 4O_{10} (OH)_8$] provides reflection with the greatest intensity $2\theta = 18.76°$ (d = 4.7 Å). The XRD results also show the crystalline form is monoclinic. The result of XRD for activated nano zeolite (Figure 3b). It showed that the mineral content is dominated by mineral quartz (SiO_2), calcite ($CaCO_3$), and reduced mineral composition clinochlore [$(Mg, Fe)_6 (Si, Al) 4O_{10} (OH)_8$]. This is because the zeolite has been through the process of activation and heating at high temperatures (Ates and Hardacre, 2012).

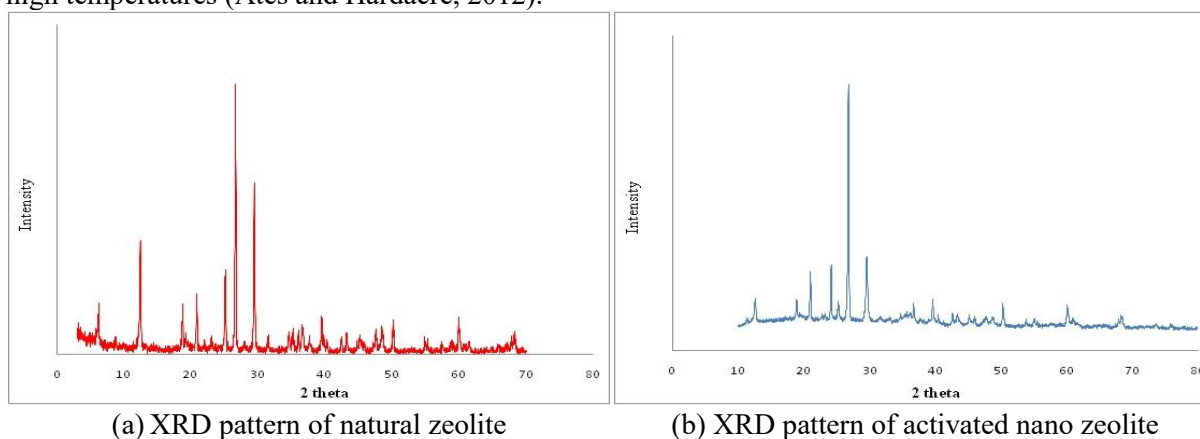(a) XRD pattern of natural zeolite   (b) XRD pattern of activated nano zeolite

Figure 3. XRD patters of zeolite before and after activated.

The characterization results using XRF (Table 2) shows the content of silica and alumina is the main composition of the zeolite. Other elements contain in the zeolite are magnesium, calcium and potassium. These elements can be exchanged with other ions, both with metal or non-metal ions. Whereas the rest elements are an impurities that occupied the zeolite pores. The impurities can be reduced by heating and chemical activation of zeolites such as by acid, base or salt treatment (Margeta et al., 2013). Ratio of Si/Al in the natural and activated nano zeolites are 3.99 and 3.87, respectively. It is clear that the ratio of Si/Al in the zeolite before and after activation did not change so much; it shows that the natural zeolite has been successfully activated without damaging the structure of the zeolite.

Table 2. Data of XRF characterization

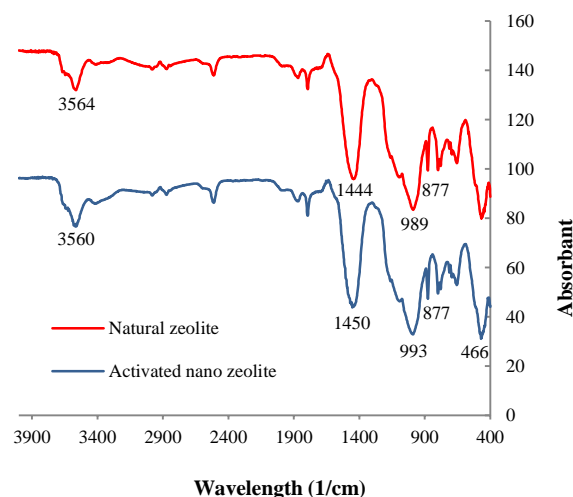| Natural nano zeolite		Activated nano zeolite	
Compound	% Weight	Compound	% Weight
SiO_2	47.32	SiO_2	39.01
Al_2O_3	10.46	Al_2O_3	8.9
Fe_2O_3	8.87	Fe_2O_3	8.21
MgO	8.84	MgO	6.96
SO_3	0.16	SO_3	0.23
K_2O	0.45	K_2O	0.36
CaO	11.54	CaO	13.9
Na_2O	0.07	Na_2O	0.11
P_2O_5	0.161	P_2O_5	0.161
TiO_2	0.377	TiO_2	0.362
Mn_2O_3	0.163	Mn_2O_3	0.146
Cr_2O_3	0.078	Cr_2O_3	0.135

Figure 4. FTIR patterns of natural and activated nano zeolites.

The characterization results using FTIR (Figure 4) showed that the natural zeolite has an early peak at 3564 cm-1 and nano zeolites after activation decreased to 3560 cm^{-1}, this represents the absorption peak of OH group is in the range 3700-1600 (Elaipoulus et al ., 2010). Decline in the peak of O-H group in the nano zeolites after activation is due to loss of water molecules inside the zeolite. This proves that the nano zeolite after activation has lower impurities than the natural zeolite. In addition, there is the peak of 877-993 cm^{-1} which is the asymmetric stretching vibration of Si-O and Al-O; interpreted the bond absorption at the main structure unit of zeolite (Barczyk et al., 2014). Therefore, the carbonate ion in the natural zeolite appears at the peak of 1444 cm^{-1} and for the activated zeolite at 1450 cm^{-1}. Wave number carbonate lies in the range of 1450-1410 cm^{-1} (Coates, 2000). The identified wave numbers recorded in this investigation compared to previous studies shown in Table 3. The results of FTIR measurements show that the functional groups contained in the sample exhibits the character of zeolite framework structure. Both zeolites, before and after activation, provide almost the same wave numbers. This may imply that the activation of zeolites (physically and chemically) did not change the basic framework of the zeolite structure group.

Table 3. FTIR spectra readings on zeolites

Functional group	Bonded	Wavelength number (cm^{-1})		
		Natural zeolite	Activated nano zeolite	Reference
Un-bonded O-H	O-H	3564	3560	3800-1600***
Carbonate ion	Ca-O	1444	1450	1450-1410**
Asymmetric stretching vibration of Si-O and Al-O	Si-O-Si and Si-O-Al	877 and 989	877 and 993	1300-800*
Bending vibration of Si-O or Al-O	Si-O or Al-O	-	466	466-439***

Source: *Elaipoulus et al. (2010); **Coates (2000); ***Barczyk et al. (2014)

4. Conclusions

Based on the results and discussions, some conclusions can be written as following:

1. Morphology of the activated nano zeolite significantly changed due to an activation process.
2. Surface area, chemical content and the basic framework of the zeolite were almost un-changed after treated by the proposed process.
3. Impurities contained in the zeolite can be reduced through activation process (physically and/or chemically) and calcination.

References

[1] Ates A and Hardacre C 2012 *J. Coll. Interface Sci.* **372** 130
[2] Barczyk K, Mozgawa, W and Król M 2014 *Spect. Acta Part A: Molecular and Biomolecular Spect.* **133** 876
[3] Coates J 2000 Encyclopedia of Analytical Chemistry ed R A Meyers (New York: John Wiley & Sons) pp 10815–10837
[4] Elaiopoulos K, Perraki T and Grigoropoulou E 2010 Microporous and Mesoporous Materials **134** 29
[5] Erdem E, Karapinar N and Donat R 2004 J. Coll. Interface Sci. **280** 309
[6] Ibrahimi M M and Sayyadi A S 2015 Int. J of Geology Agric. Env. Sci. **3** 1
[7] Izci E and Izci A 2007 Turkish J. Chemistry **31** 523
[8] Lestari D Y 2010 Prosiding Seminar Nasional Kimia dan Pend. Kimia 2010 (Yogyakarta) p 1 (in Indonesia)
[9] Margeta K, Logar N Z, Šiljeg M and Farkas A 2013 *Natural zeolites in water treatment –how effective is their use (Water Treatment)* ed W Elshorbagy and R K Chowdhury (Rijeka: InTech) chapter 5 pp 81-112
[10] Mirzaei N, Hadi M, Gholami M, Fard R F and Aminabad M S 2016 *J. the Taiwan Inst. Chem. Eng.* **59** 186
[11] Motsi T, Rowson N A and Simmons M J H 2009 *Int. J. Mineral Process.* **92** 42
[12] Noroozifar M, Khorasani-Motlagh M and Naderpour H 2014 *Microporous and Mesoporous Materials* **197** 101
[13] Utubira Y, Wijaya K, Triyono and Sugiharto E 2006 *Indo. J. Chem.* **6** 231
[14] Wang S and Peng Y 2010 *Chem. Eng. J.* **156** 11