



Studies of Modification of Zeolite by Tandem Acid-Base Treatments and its Adsorptions Performance Towards Thorium

G. Nurliati^{1,2*}, Y.K. Krisnandi², R. Sihombing² and Z. Salimin¹

¹Center for Radioactive Waste Technology, National Nuclear Energy Agency, Puspipstek Area Serpong, Tangerang 15310, Indonesia

²Department of Chemistry, University of Indonesia, Depok 16424, Indonesia

ARTICLE INFO

Article history:

Received 26 January 2015

Received in revised form 20 May 2015

Accepted 21 May 2015

Keywords:

Natural zeolite

Tandem acid-base treatments

Hierarchical materials

Thorium adsorption

ABSTRACT

Hierarchical zeolite was prepared from natural zeolite using tandem acid-base treatments and applied as adsorbent for Th(IV) removal. Natural zeolite occurred naturally as microporous material. It was modified using two familiar methods simultaneously, dealumination and desilication techniques, to change its micropore size into hierarchical pores. Extensive characterization of both natural and modified zeolites were conducted using XRD, BET, SEM-EDS, and AAS. XRD Patterns of raw, pre-treated, and acid-base tandem modified zeolites show that the modification process has not changed the crystal properties of this material. However, the Si/Al ratio is increased from 6.688 to 11.401 for Na-zeolite (NaZ) and modified zeolite, ZA2B respectively. The surface area is increased from 125.4 m²/g (NaZ) to 216.8 m²/g (ZA2B), indicative of the creation of mesopore in addition to naturally micropore structure. The application of these zeolite materials as adsorbent were carried out using solution of 50 ppm Th⁴⁺ measured using UV-Vis spectrophotometer. The UV-Vis result shows that the modified zeolite (ca. 10 mg) has higher adsorption capacity than natural zeolite. The adsorption process does not fit into Langmuir and Freundlich isotherm and the adsorption capacity of this material increase from 909 mg/g to 2000 mg/g for NaZ and ZA2B respectively.

© 2015 Atom Indonesia. All rights reserved

INTRODUCTION

Indonesia is rich with a large amount of minerals including natural zeolites. Zeolite is an aluminosilicate material with three-dimensional frameworks that consist of SiO₄ and AlO₄ tetrahedra arranged regularly in which each oxygen atom is shared between two tetrahedra [1]. The replacement of Si⁴⁺ with Al³⁺ in tetrahedral structure creates negative formal charge and counterbalanced by exchangeable cations (e.g., Na⁺, K⁺, Ca²⁺, Mg²⁺) [2].

The structure of Zeolite is filled with cavities and channels with dimensions ranging from 0.2 nm to 1 nm (micropores) inside which water molecules and counterions may reside [3]. Small ions and

molecules can pass through these channels but large ions and molecules are excluded. Due to its microporosity and relatively high surface area, natural zeolites have been widely used as adsorbents, ion exchanger, catalysts, and separation media [1].

Despite its wide applications, natural zeolite has limitations due to (1) undesired impurity in its structure, and (2) its properties which are not optimized by nature [3]. These limitations can be overcome by modifications of the structure of natural zeolite. Dealumination and desilication are commonly employed to change the properties of natural zeolite such as Si/Al ratio, acidity, and pore size [3,9,13].

Dealumination is a process in which the framework aluminum atoms are removed without destroying the micropore structure. It can be achieved by hydrolysis of the Al-O-Si bonds using

* Corresponding author.

E-mail address: gustri@batan.go.id

DOI: <http://dx.doi.org/10.17146/aij.2015.382>

two common methods, i.e., thermal treatment (commonly by steaming) [4] or acid leaching [5]. Dealumination changes the Si/Al ratio in zeolite, hence affecting the surface and acidic properties of zeolite [6]. The desilication process, where it is the silicon atoms which are removed, follows the same pattern as dealumination such as type of lattice defects and mesopore formation. The difference lies in the use of alkaline solution for leaching method [7-9]. Desilication can introduce mesoporosity to zeolite through alkaline treatment [10-12]. J.C. Groen in Huang (2014) suggested that for mordenite with optimal Si/Al ratios (20–30), mesoporosity was introduced after it was subjected to alkaline treatment (0.2 M NaOH at 65°C for 30 min).

Recently, combinations of dealumination and desilication techniques have been employed in order to modify zeolite through mesopore formation [13-15]. Van Laak (2010) found that sequential acid-alkaline treatments of mordenite zeolites (Si/Al = 8–15) are effective for mesopore formation. Our research group [15] has conducted modification of zeolite by combining acid-base treatments to the natural zeolite from Lampung-Indonesia in order to introduce mesoporosity, and studied its capacity to adsorb Cu(II) from aqueous solution. The results show that acid-base treatments enhanced the surface area of the natural zeolite from Lampung-Indonesia by 350% and the adsorption capacity increase by 24%.

Based on the previous work, the aims of this research are to modify natural zeolite from Bayat-Klaten, Central Java, Indonesia, by tandem acid-base treatments, and to study the effect of modification on thorium adsorption. Thorium is a naturally occurring radioactive element widely distributed over the earth's crust with a half life of 1.39×10^{10} years. Thorium has been extensively used in various application such as light bulb elements, lantern mantles, welding electrodes, and heat-resistant ceramics. Due to its stability at ambient temperature, the direct toxicity of thorium is low. However when living organisms are exposed to thorium nitrate, thorium precipitates in a hydroxide form and is mainly localized in liver, spleen and marrow [1]. Different types of materials have been used as adsorbents for thorium, such as activated carbons and zeolites [1], perlite [16], modified clays MTTZ derivative [17], poly(methacrylic acid)-grafted chitosan/bentonite composite [18], Na-bentonite [19], Al-pillared bentonite [20], and cation exchanger resin [21]. But no data were available for its adsorption on tandem acid-base modified zeolite.

EXPERIMENTAL METHODS

Modification of natural zeolite

The modification of natural zeolite from Bayat-Klaten consists of physical activation, pre-treatment, Na-exchange treatment, and post-modification by tandem acid-base treatments.

The activation of natural zeolite was performed by washing the zeolite with demineralized water (1:3 w/v) under stirring for 3 hours. The solid phase was dried at 300°C. The aim of physical activation is to remove water molecules from the voids of zeolite and open the zeolite's active sites.

The pre-treatment process was conducted following Ming and Dickinson [2]. The activated natural zeolite was treated with 1 M NaOAc buffer to reach a pH of 5; mixing with 30% H₂O₂ and dithionite-citrate-bicarbonate to remove free carbonates, organic matters, and free iron oxides, respectively. After pre-treatment, the counterbalanced cations in zeolite were converted into sodium ions using 0.5 M NaCl solution (10 g zeolite/100 ml solution) at 80°C under stirring for 2×8 hours.

Post-modification was started with dealumination process, by stirring Na-zeolite in 0.6 M HCl solution (10 g zeolite/100 ml solution) at 100°C for 2 hours (under reflux condition). The solid phase was washed with demineralized water and dried at 65°C. Desilication was conducted by stirring zeolite in 0.2 M NaOH solution (3.3 g zeolite/100 ml solution) at 65°C for 30 minutes. The zeolite samples were then labeled as follow: Raw Zeolite (RZ), Pretreatment Zeolite (PZ), Na-Zeolite (NaZ), 1 Acid treated zeolite (ZA1), 2 acid treated zeolite (ZA2), Acid-base treated zeolite (ZA2B), and base treated zeolite (ZB1). Characterization for raw and modified zeolites were conducted with X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), atomic absorption spectroscopy (AAS), and surface area analysis including Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods.

Sorption studies

Kinetic studies of adsorption were performed with 50 ppm Th(IV) solution. About 0.1 g zeolite was mixed with 10 ml solution and placed in a shaker for a certain time interval. The adsorbent was then removed by centrifugation and filtration, while the thorium concentration was determined using UV-Vis spectrometer.

The isotherm studies were conducted with the same process as in the kinetic study by varying concentration of thorium solution in the range of 5-100 ppm and the mixture was shaken for optimum adsorption time obtained from the kinetic study.

RESULTS AND DISCUSSION

The natural zeolite and its derived sample, modified with 0.6 M HCl, 0.2 M NaOH, before and after tandem acid-base treatment, were characterized with X-ray diffraction (XRD). The 2θ values in Fig. 1 show that the main composition of natural zeolite from Bayat-Klaten are mordenite ($2\theta = 9.79^\circ; 22.37^\circ; 25.63^\circ; 27.24^\circ$ and 27.76°) and heulandite ($2\theta = 9.85^\circ; 22.21^\circ; 22.34^\circ; 25.96^\circ; 28.09^\circ$). The figure shows that there were no significant changes in the XRD patterns before and after treatments. It confirms that the structure of mordenite and heulandite are preserved despite being treated tandemly with acid and/or base. Huang (2014) showed similar results to this work. The sequential steaming-acid leaching-alkaline treatments did not affect the crystallinity of as-synthesized mordenite zeolite from China. Further characterization with energy-dispersive X-ray spectroscopy (EDS) (Table 1) shows that the dominant exchangeable cation in natural zeolite structure from Bayat-Klaten is Ca^{2+} , indicative of natural zeolite from Bayat-Klaten which is Ca-mordenite and Ca-heulandite type.

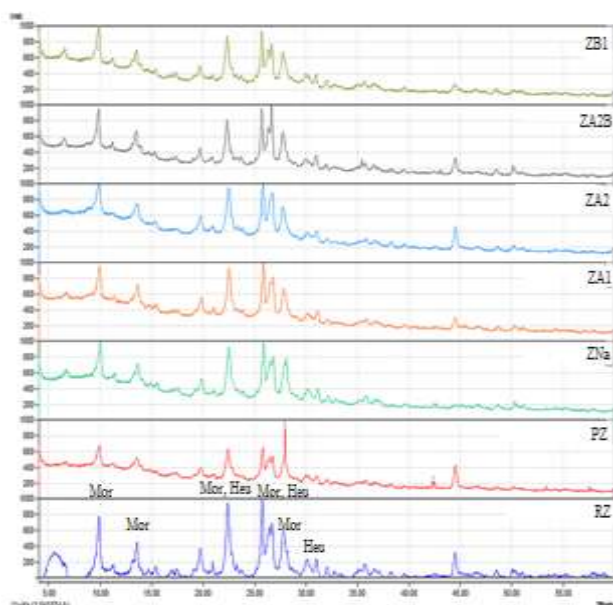


Fig. 1. XRD spectrum of raw natural zeolite and modified zeolite from Bayat-Klaten.

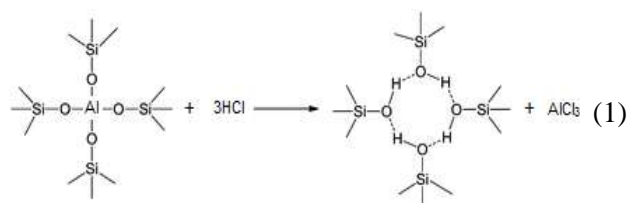
Table 1. Characterization of raw natural, NaZ and ZA2B-form zeolite from Bayat-Klaten using EDS

Element	% Mass		
	Raw Zeolite	NaZ	ZA2B
C	9.52	14.39	10.17
O	53.10	52.33	52.10
Na	0.86	2.16	3.54
Mg	0.52	0.13	0.13
Al	5.95	4.73	4.63
Si	25.72	24.40	28.26
K	0.57	0.33	0.41
Ca	1.92	0.69	0.36
Fe	1.84	0.83	0.39

Post-modification treatments

In this experiment, acid treatment causes dealumination of the zeolites, in which Al-O bonds are weakened by proton attack causing skeletal vacancies and defects. The vacancies and defects enlarge the pore openings of the zeolite, increasing the surface area and adsorption ability [22].

The dealumination process can be divided into three steps: 1) cleavage of O-Al-O bonds, 2) removal of Al atom leaving atomic gaps and silanol nest, and 3) refilling of empty spaces by Si atoms. The suggested reaction in dealumination process is showed in equation (1) [23].



Characterization using FTIR shows stretching vibration of silanol groups at 3750 cm^{-1} and OH stretching band from silanol groups at $3540-3650 \text{ cm}^{-1}$. Characteristic lattice vibrations of the zeolitic structure can be distinguished from these band: H-O-H bending band at 1630 cm^{-1} , asymmetric stretching vibrations band at $950-1025 \text{ cm}^{-1}$ and $1050-1250 \text{ cm}^{-1}$, symmetric stretching vibrations bands at $750-820 \text{ cm}^{-1}$ and $650-750 \text{ cm}^{-1}$, double ring vibrations at $500-650 \text{ cm}^{-1}$, T-O bending vibrations at $420-500 \text{ cm}^{-1}$, and pore opening vibrations at $300-420 \text{ cm}^{-1}$ [24, 25].

Dealumination process cause wave number shifting in asymmetric stretching of the tetrahedral atoms band to the higher number. Figure 2 shows asymmetric stretching increase from 1048.72 cm^{-1}

for raw zeolite to 1054.84 cm⁻¹ and 1065.04 cm⁻¹ for NaZ and dealuminated zeolite (ZA1), respectively. This shifting is caused by the leaching of Al from zeolite framework and changes on the bond strength and Si-O-Si angle [26]. Since Si has higher electronegativity than Al and Si-O bond is shorter than the Al-O bond, the decrease of Al content causes the increase of Si-O bond strength.

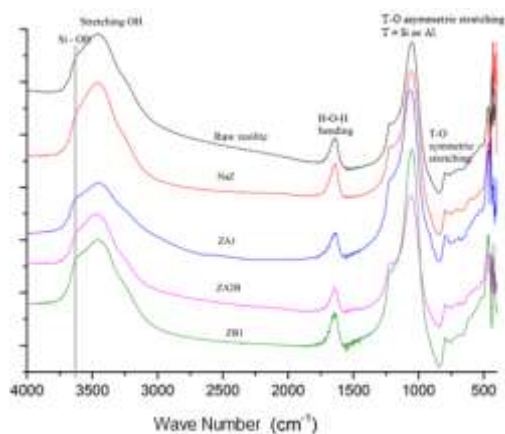


Fig. 2. FTIR spectrum of natural zeolite and its modified forms.

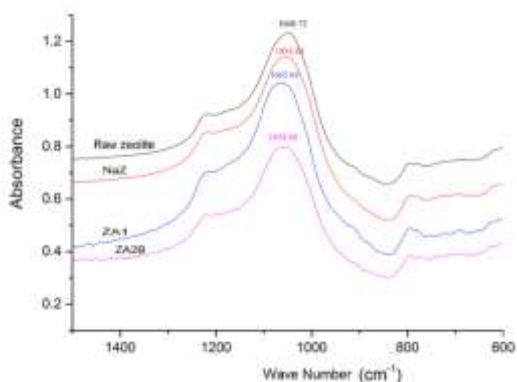


Fig. 3. Wave number shifting in natural zeolite and its modified form (enlargement of fig. 2).

The removal of Al atom from zeolite framework increase the Si/Al ratio of modified zeolite. Characterization of natural zeolite and its modified form using Atomic Absorption Spectroscopy (Table 2) shows that the Si/Al ratio after the first dealumination increase from 6.688 to 11.031 for NaZ and ZA1 respectively. The second dealumination also increase the Si/Al ratio to 14.265 for ZA2. This result indicates that the dealumination process is successful, because the amount of aluminium in the structure is decreased (by 53.6%).

The next step is alkaline treatments on both Na-exchanged and acid-treated zeolites. The aim of this treatment is to leach Si atoms from zeolite

structure and introduce mesoporosity. Alkaline treatments increase the % mass of Si, but overall decreases the Si/Al ratio of both NaZ (from 14.265 to 11.401 for ZA and ZA2B, respectively) and ZA2 (from 6.688 to 4.4715 for NaZ and ZB1, respectively). The Si/Al ratio can affect the mesopore formation in zeolite. Groen *et al.* in Silaghi [27] found that the optimal Si/Al ratio for introducing mesoporosity to zeolite framework is ~20-50. Below this ratio, only limited mesopore formation occurred since the aluminium atoms prevent Si extraction from the zeolite framework.

Table 2. Si/Al ratio of natural zeolite and its acid-base treated derivatives analysed using AAS

Zeolite	% mass Na	% mass Si	% mass Al	Si/Al
Raw zeolite	1.515	79.100	7.085	11.164
Z-pre treatment	1.920	63.200	6.825	9.260
Na-Z ^a	3.675	73.000	10.915	6.688
ZA1 ^b	3.925	76.200	6.908	11.031
ZA2 ^c	1.200	72.250	5.065	14.265
ZA2B ^d	1.610	74.050	6.495	11.401
ZB1 ^e	4.040	71.450	15.155	4.715

^asodium homoionic form of zeolite, ^bfirst dealuminated zeolite, ^csecond dealuminated zeolite, ^dtandem acid-base treated zeolite, ^ebase treated zeolite.

Structural changes caused by desilication can be observed by FTIR (Fig. 2). The intensity of the characteristic silanol band (at 3500 cm⁻¹) decreased in desilicated zeolite. This infrared characteristic is known as defect sites in zeolite. Therefore it can be deduced that alkaline attack mostly occurred in these defect sites.

The surface area, isotherm adsorption and pore distribution of zeolite were determined by Brunauer-Emmett-Teller (BET) method. Table 3 shows the enhancement of surface area of the zeolite: from 125.4 mg² g⁻¹ (NaZ) to 138.0 and 216.8 mg² g⁻¹ for alkaline treated zeolite, ZB1 and ZA2B respectively. It indicates that alkaline treatments could introduce mesoporosity in natural zeolite.

Table 3. BET characterization of raw zeolite and its modified forms

Zeolite	S _{ext} ^a (m ² g ⁻¹)	V _{micro} ^b (cc g ⁻¹)	V _{total} ^c (cc g ⁻¹)	V _{meso} ^d (cc g ⁻¹)	R _{micr o} ^e (nm)
Raw zeolite	140.0	0.05934	0.1357	0.07636	0.62
NaZ	125.4	0.04642	0.1109	0.06448	1.02
ZA1	120.6	0.04864	0.1395	0.09086	0.66
ZB1	138.0	0.05773	0.1326	0.07487	td
ZA2B	216.8	0.09795	0.1804	0.08245	0.52

^aMultipoint BET, ^bt-method, ^cat P/Po = 0.992594
^dV_{total}-V_{micro}, ^eDA method pore radius (mode)

The N₂ isotherm adsorption of zeolite and its modified zeolite forms in Fig. 4 shows that there is hysteresis loop in the isotherm adsorption curve of desilicated zeolite ZA2B and ZB1 (Fig. 4 (d) and (e)). The curve is following IUPAC isothermal curve type four, which indicated there are capillary condensation in mesoporous material [28].

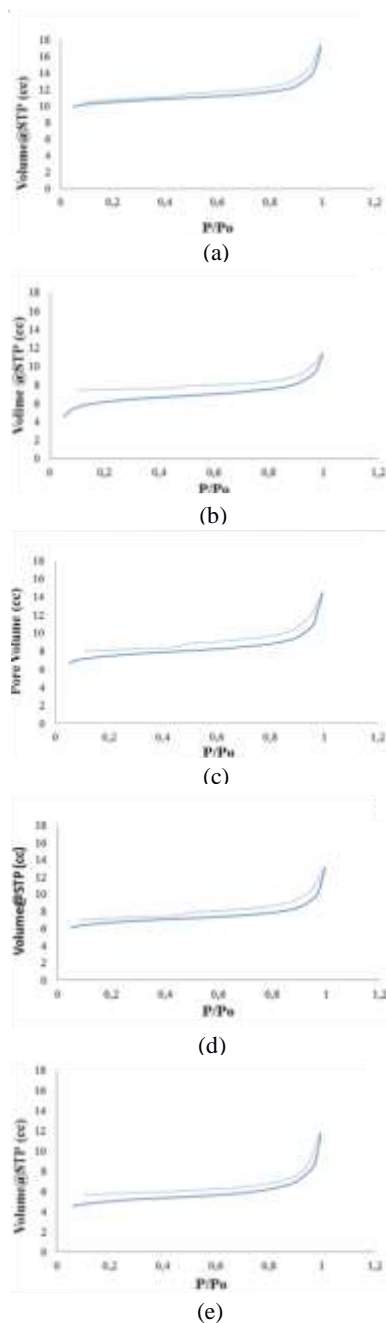


Fig. 4. Nitrogen isotherm adsorption curve of natural zeolite and its modified forms, (a) Raw zeolite, (b) NaZ, (c) ZA1, (d) ZB1, (e) ZA2B (bold line):adsorption (dash line): desorption.

Barrett-Joyner-Halenda (BJH) analysis shows the pore size distribution in zeolite. Figure 5 (a) shows that pore size (diameter, Ø) distribution in raw zeolite is < 2 nm as well as in NaZ

(Fig. 5 (b)), ZA1 (Fig. 5 (c)) and ZB1 (Fig. 5 (d)). While in ZA2B (Fig. 5 (e) and enlarge in Fig. 6), pore size distribution lies in $d < 2$ nm and 2-8 nm. The existence of 2-8 nm pores indicated that tandem acid-base treatments can introduce mesoporosity in zeolite, leading to the hierarchical structure of zeolites.

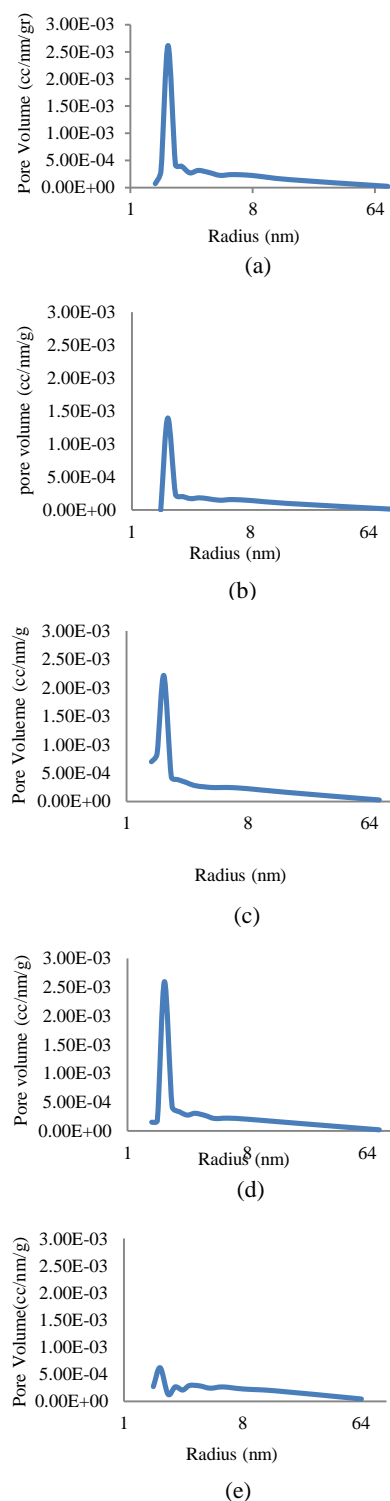


Fig. 5. BJH desorption curve of natural zeolite and its modified forms (a) Raw zeolite, (b) NaZ, (c) ZA1, (d) ZB1, (e) ZA2B.

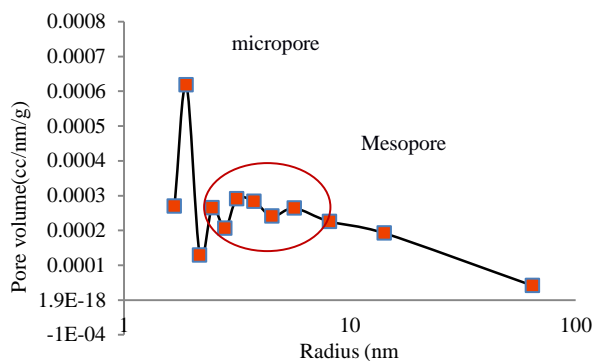


Fig. 6. BJH desorption curve of ZA2B (enlargement of Fig. 5).

Figure 7 (a) suggests that the schematic mechanism of optimal mesopore formation in zeolite upon alkaline treatment. Since the Si/Al ratio of parent zeolite (ZA2) used for desilication process is below 20, the Al atoms prevent Si extraction hence the formation of mesopore ($\phi > 2$ nm) in this work is limited, as illustrated in Fig. 7 (b).

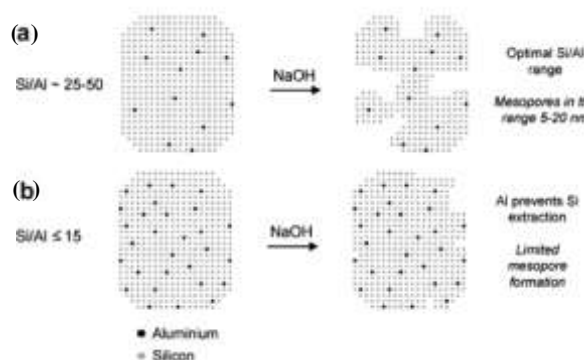


Fig. 7. The schematic mechanism of mesopore formation in zeolite upon alkaline treatment (extracted from [21]).

Sorption studies

This sorption studies focused on the removal of thorium. The aim of this experiment was to determine the optimum adsorption time and the adsorption capacity of zeolites before and after modification. UV-vis spectrometer analysis (Fig. 8) shows that the optimum time for adsorption of 50 ppm Th(IV) solution is 120 minutes for both NaZ and ZA2B. Furthermore, it can be seen that after 180 minutes the adsorption capacity tends to decrease, especially for the modified zeolite, namely ZA2B. This indicates that some Th^{4+} was leaching from the zeolite, possibly because the concentration equilibrium between Th^{4+} inside and outside zeolite may be shifted.

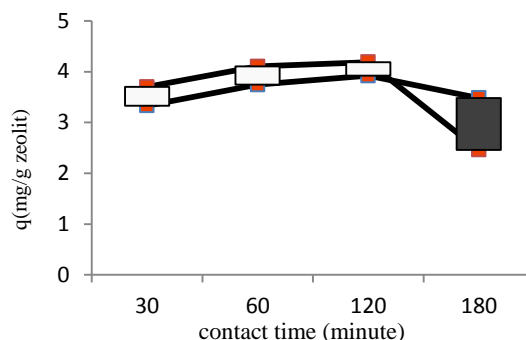


Fig. 8. UV-vis spectrometer analysis for determination of optimum contact time in adsorption of Th(IV) by NaZ (bold line) and ZA2B (dash line).

The determination of the adsorption capacity of zeolite was conducted by varying the concentration of thorium and contacting the thorium-containing solution with zeolite for 120 minutes. Figure 9 shows that adsorption capacity of acid-base treated zeolite (ZA2B) is slightly higher than sodium homoionic form (NaZ). Because the initial concentration of thorium solution used was relatively low (only up to 100 mg/L) then the difference was not significant and the adsorption had not reached saturation (as can be seen in Fig. 9 the adsorption curves are still increasing and had not reached a plateau). Nevertheless, the acid-base-treated zeolite removed higher quantities of thorium because of its larger framework channels and their higher number of ion-exchange sites.

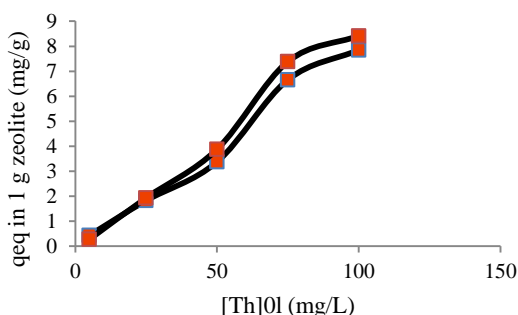


Fig. 9. UV-Vis characteristic of Th(IV) adsorption by NaZ (bold line) and ZA2B (dash line).

To determine the adsorption capacity quantitatively, the isotherm data are fitted to different isotherm adsorption models. Adsorption isotherm describes the equilibrium of liquid adsorption on solid surface. Two commonly used adsorption isotherm models on solid surface are the Langmuir and Freundlich models. The Langmuir equation shown in eq (2) [29]:

$$\frac{C_{eq}}{q} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m} \quad (2)$$

C_{eq} is ion concentration in equilibrium solution (mg/L or mmol/L), q is adsorption per gram of adsorbent which is obtained by dividing the amount of adsorbate by the weight of the adsorbent (mg/g or mmol/g) and q_m is adsorption capacity (mg/g or mmol/L). Hence, if a graph of C_{eq}/q is plotted against C_{eq} , it will be a straight line, and adsorption capacity is $1/\text{slope}$.

The Freundlich equation is shown in eq (3):

$$\text{Log } q_e = \text{log } K_F + 1/n \text{ log } C_e \quad (3)$$

n is a constant value related to adsorption energy. K is a constant value related to adsorbent capacity.

Figure 10 shows that R-square value of both Langmuir and Freundlich isotherm model are far from the expected value (ca. 1). It means that the adsorption of thorium in zeolite does not fit in both isotherm models.

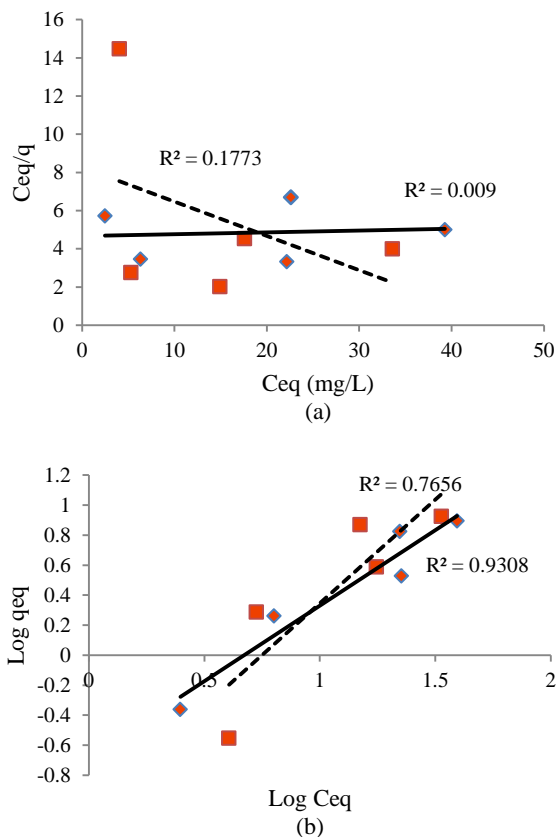


Fig. 10. Linearization of Langmuir isotherm (a) and Freundlich isotherm (b) NaZ (bold line) and ZA2B (dash line).

To determine adsorption capacity, equation 4, that is modified from equations in Langmuir and Freundlich isotherm models, is used instead [29].

$$\frac{C_{eq}^{1/n}}{q} = \frac{1}{q_m b} + \frac{C_{eq}^{1/n}}{q_m} \quad (4)$$

If $C_{eq}^{1/n}/q$ is plotted against $C_{eq}^{1/n}$, a straight line arises, hence the adsorption capacity is proportional with $1/\text{slope}$.

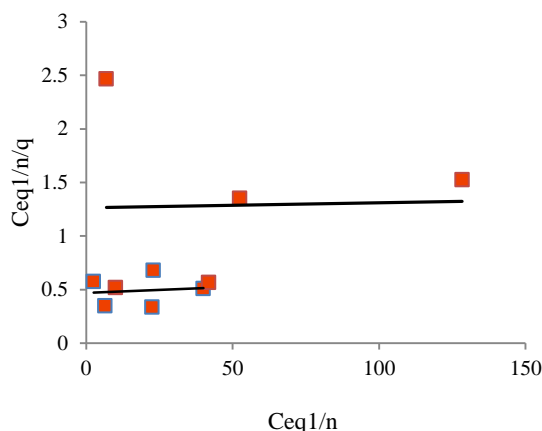


Fig. 11. Langmuir-Freundlich isotherm adsorption by NaZ (bold line) and ZA2B (dash line).

The adsorption capacity of both zeolites (NaZ and ZA2B) shows in Table 4 indicate that tandem acid-base treatments of natural zeolite from Bayat-Klaten (ZA2B) can improve its adsorption capacity significantly, by as high as ca. 120%, compared to its homoionic form (NaZ). This result is higher than previous work of our research group [15].

Talip *et al.* [16] used expanded perlite to adsorb thorium from aqueous solution and found that its maximum thorium uptake capacity was $84 \pm 4\%$ and the adsorption reached equilibrium within 60 minutes. Guerra *et al.* [17] modified diquite and bentonite mineral samples from the Amazon region, Brazil with MTTZ derivative (5-mercapto-1-methyltetrazole) and the modification increased the thorium removal rate to 13% and 9% for diquite and bentonite respectively (The degree of reaction was estimated 80% for D_{MTTZ} and 65% for B_{MTTZ} samples). Kaygun *et al.* [30] modified clinoptilolite (CLI) from Turkey with polyacrylonitrile (PAN) and found the equilibrium as 97.97% sorption of thorium (IV) solution was reached within 45 minutes. Metaxas *et al.* [1] compared thorium removal by different adsorbents, i.e. two types of activated carbons extracted from olive pulp (carbon ACOP) and olive stone (carbon ACO), two types of natural zeolites (Na-CLI and Na-MOR), and two types of synthetic zeolites (NaX and NaA). They found that percentage thorium removal for carbon ACOP, carbon ACO, Na-CLI, Na-MOR, NaA and NaX were 70.30%, 42.5%, 14.55%, 37.65%, 50.40%, and 71.15%, respectively. The percentage thorium removal from this work were 71.5% for NaZ and 76.5% for ZA2B. Thus, it can be seen that modification of zeolite

from Bayat-Klaten has higher adsorption capacity than Na-CLI, Na-MOR, NaX, NaA, activated carbons, and modified bentonite with MTTZ. This might be caused by the acid-base treatments increasing the zeolite's framework channels and ion-exchange sites. But it has a lower removal capability than manufactured expanded perlite, CLI(PAN), and modified diquite with MTTZ. This is probably because the manufactured expanded perlite has uniform active sites and the presence of MTTZ molecules which are intercalated in the diquite structures enhanced its surface area significantly (from $25 \text{ m}^2\text{g}^{-1}$ to $178.8 \text{ m}^2\text{g}^{-1}$) while composite material such as CLI(PAN) have better selectivity for the capture of thorium ions, and smaller solubility in water than the respective inorganic compound [30]. However, as the manufactured adsorbents undergo a certain process to get into the final form, the cost-effectiveness of using each of these groups of adsorbents should be considered in addition to the simplicity of modification procedure and the abundance of the inorganic materials in nature. Thus, tandem acid-base treatment is a simple, effective and economical procedure to modified natural zeolite as thorium adsorbent. The comparison of thorium uptake capacity on different adsorbents is given graphically in Fig. 12.

Table 4. Adsorption capacity of thorium using natural zeolite

Zeolite*	Slope	Adsorption capacity (mg/g)
NaZ	0,0011	909
ZA2B	0,0005	2000

NaZ: homoionic form zeolite
ZA2B: tandem acid-base treated zeolite

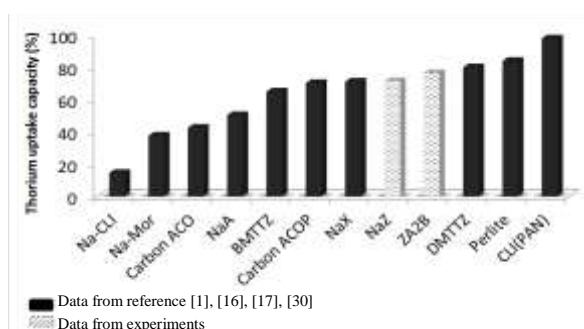


Fig. 12. The comparison of thorium uptake capacity on different adsorbents.

CONCLUSION

The modification of natural zeolite from Bayat-Klaten using tandem acid-base treatments has successfully introduced mesoporosity in zeolite

framework providing hierarchical porosity, thus improving its properties. Dealumination treatment decreased the amount of aluminium in the structure by 53.6% and changed the Si/Al ratio of zeolite to 14.265. Desilication treatment increased the surface area of zeolite by 72.9% and introduced mesoporosity in the zeolite framework. This preliminary study shows that hierarchical porosity plays an important role in the adsorption capacity of zeolite. The tandem method is shown as a potential technique for modifying natural zeolites that could give them added value and functions.

To conclude, the sorption studies show that the thorium ion adsorption capacity of acid-base treatments zeolite (ZA2B) is 120% higher than that of the sodium homoionic form (NaZ). Further work should be carried out to study the stability of thorium-filled hierarchical zeolite in matrix so that this work can be useful in handling aqueous radioactive wastes through immobilization process.

ACKNOWLEDGMENT

We thank Bambang Sugeng, Dr. Adel Fisli, and Sugeng Purnomo S.ST from National Nuclear Energy Agency for help in XRD, BET, and AAS analysis, respectively.

REFERENCES

1. M. Metaxas, V. Kasselouri-Rigopoulou, P. Galiatsatou *et al.*, *J. Hazard. Mater.* **B97** (2003) 71.
2. D.W. Ming and J.B. Dixon, *Clays Clay Miner.* **35** (1987) 463.
3. J. Weitkamp, *Solid State Ionic* **131** (2000) 175.
4. M. Muller, G. Harvey and R. Prins, *Microporous Mesoporous Mater.* **34** (2000) 135.
5. M. Boveri, C. Marques-Alvarez, M.A. Laborde *et al.*, *Catal. Today* **114** (2006) 217.
6. M.D. González, Y. Cesteros and P. Salagre, *Microporous and Mesoporous Mater.* **144** (2011) 162.
7. F.C. Meunier, D. Verboekend, J.P. Gilson *et al.*, *Microporous and Mesoporous Mater.* **148** (2012) 115.
8. W.C. Yoo, X. Zhang, M. Tsapatsis *et al.*, *Microporous and Mesoporous Mater.* **149** (2011) 147.

9. V. Paixão, A.P. Carvalho, J. Rocha *et al.*, *Microporous and Mesoporous Mater.* **131** (2010) 350.
10. K. Sadowska, K. Góra-Marek, M. Drozdek *et al.*, *Microporous and Mesoporous Mater.* **168** (2013) 195.
11. V. Paixão, R. Monteiro, M. Andrade *et al.*, *Applied Catalysis A: General* **402** (2011) 59.
12. B. Gil, Ł. Mokrzycki, B. Sulikowski *et al.*, *Catalysis Today* **152** (2010) 24.
13. A.N.C. van Laak, S.L. Sagala, J. Zecevic *et al.*, *J. Catal.* **276** (2010) 170.
14. S. Huang, X. Liu, L. Yu *et al.*, *Microporous and Mesoporous Mater.* **191** (2014) 18.
15. D.Y. Christine, Preparation and Characterization of Mesopore Zeolite from Natural Zeolite using Tandem Acid-Base Treatments, Undergraduate Thesis, University of Indonesia (2014). (in Indonesian)
16. Z. Talip, M. Eral and Ü. Hiçsönmez, *Journal of Environmental Radioactivity* **100** (2009) 139.
17. D.L. Guerra, R.R. Viana and C. Airoidi, *Hazardous Materials* **168** (2009) 1504.
18. T.S. Anirudhan, S. Rijith and A.R. Tharun, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **368** (2010) 13.
19. Duo-qiang Pan, Q. Fan and P. Li, *Chemical Engineering Journal* **172** (2011) 898
20. E.S. Wulandari, Utilization of Aluminium Pilared Bentonite in the Treatment of Thorium Waste from Mantle Lantern Fabrication, Undergraduate Thesis, Nuclear Technology Academy (2011). (in Indonesian)
21. A.G.S. Nainggolan, Adsorbtion of Thorium from Contaminated Lantern Mantle Waste Soils with Cation Exchange Resin and its Immobilization with Polimer, Undergraduate Thesis, Diponegoro University (2011). (in Indonesian)
22. X. Wang, O. Ozdemir and M.A. Hampton, *Water Research* **46** (2012) 5247.
23. R. Meilani, Activity and Stability of Dealuminated Natural Zeolite from Lampung (with HCl and HF) on Etanol Dehidration Reaction, Undergraduate Thesis, University of Indonesia (1999). (in Indonesian)
24. J. Jiao, Quantitative Characterization of Aluminum in Non-hydrated Zeolite Catalysts by Multi-nuclear Solid-state NMR Spectroscopy, Ph.D Thesis, Stuttgart University (2006).
25. G.E. Christidis, D. Moraetis and E. Keheyan, *Applied Clay Science* **24** (2003) 79.
26. F. Cakicioglu-Ozkan, *Microporous and Mesoporous Materials* **77** (2005) 47.
27. M.C. Silaghi, C. Chizallet and P. Raybaud, *Microporous and Mesoporous Mater.* **191** (2014) 82.
28. S. Octaviani, Synthesis and Characterization of ZSM-5 Mesopore Zeolite with Desilication Method and Preliminary Study of Oxidation Catalysist of Methane, Undergraduate Thesis, University of Indonesia (2012). (in Indonesian)
29. U.T. Santoso, D. Umaningrum, U. Irawati *et al.*, *Indo. J. Chem.* **8** (2008) 177. (in Indonesian)
30. A.K. Kaygun and S. Akyil, *Journal of Hazardous Material* **147** (2007) 357.