Indonesian Journal of Computing, Engineering, and Design

Journal homepage: http://ojs.sampoernauniversity.ac.id/index.php/IJOCED

Lean Condition Procedure for Utilization of Silica from Rice Husk as Zeolite Precursor

W. Kurniawan [1], H. Hinode [2]*

[1] Departement of Transdisciplinary Science and Engineering, School of Environment and Society, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

[2] Emeritus Professor, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Correspondence: E-mail: kurniawan.w.ab@m.titech.ac.jp

ABSTRACT

Rice husk is rich in Si that makes it applicable as Si source for zeolite synthesis. However, the conventional method to use rice husk as a zeolite precursor has some drawbacks, which are: Si recovery method that involves burning and causing air pollution and carbon resources loss; and the use of severe conditions and sophisticated apparatuses which are not suitable for rural application where rice husk is mainly produced. In this paper, a method to prepare rice husk as zeolite Si source via a non-combustion process was proposed. Furthermore, its utilization as a zeolite precursor via moderate condition was also investigated. Si was recovered directly from rice husk using a sodium hydroxide solution. Si was successfully recovered from rice husk, and the optimum condition for recovery was found to be 1 N of NaOH and 16 hours of contact time. The application of the recovered Si for zeolite precursor at moderate condition was successful, and it was able to produce a product rich in zeolite P and zeolite X depending on the condition. Among zeolites synthesized in this experiment, the sample prepared by treatment time of 15 hours showed the highest cation exchange capacity, which makes it a promising material to be used as an ion-exchange agent.

ARTICLE INFO

Article History:
Received 07 Aug 2020
Revised 31 Aug 2020
Accepted 12 Sept 2020
Available online 01 Oct 2020

Keywords:
Rice husk,
Waste utilization,
Zeolite.

1. INTRODUCTION

Rice is one of the major staple foods in the world with annual global production of 501.2 million tons (Food and Agricultural Organization of the United Nations, 2017). This high production is accompanied by the generation of waste in the form of rice husk, which according to the paddy composition data by (Soltani et al., 2015) would amount to around 125 million tons per year. Meanwhile, for the case of Indonesia, the rice annual production was 37.1 million tons, which translates to the generation of rice husk waste of around 9 million tons (United States Department of Agriculture, 2019). This high volume of waste will cause an adverse environmental problem if it is not addressed properly. Solutions were proposed, ranging from incineration to utilization, which includes application as construction material and biomass fuel (Ding et al., 2014; Santasnachok et al., 2015). These proposed solutions were able to utilize rice husk in a large quantity. However, they still could not utilize the potency possessed by rice husk to the fullest. It is then necessary to explore other potential usages of rice husk.

Rice husk contains a high amount of Si and carbon (Soltani et al., 2015), thus, it can also be viewed as unused resources. Si and carbon materials possess high functionality and wide applications, and rice husk is a promising material to be used as a precursor for those kinds of material. Research had been done to apply rice husk for this purpose, such as the utilization of rice husk Si content to synthesize zeolite or mesopores silica. Zeolite is a porous aluminosilicate mineral that can purify water containing harmful mineral due to its ion exchange capability. There are many type of zeolites such as zeolite A, X, and P, and each type of zeolite has different structure and ion exchange capability.

Some researches have successfully developed procedures to utilized rice husk as zeolite precursors (Carmona et al., 2013; Dey et al., 2012; Mohamed et al., 2015; Prasetyoko et al., 2006). Our research group had also successfully synthesized high purity zeolite A and X from rice husk ash and applied them for cadmium removal (Purnomo et al., 2012; Santasnachok et al., 2015). Nonetheless, these developed procedures still contain some drawbacks. One of the drawbacks is in the Si recovery step. To recover Si from rice husk, the conventional procedures apply burning to remove carbon content, which causes air pollution by the release of carbon dioxide and particulate matter, as well as a loss of energy and carbon resources due to biomass burning. Moreover, to increase the quality of the obtained Si precursor via these procedures, controlled combustion and pretreatment such as acid washing is necessary, which add to the total cost of synthesis. The disadvantage of loss of energy can be minimized by using rice husk as biomass fuel and apply the resulting rice husk ash as Si source. However, the obtained rice husk ash often contains a considerable amount of residual carbon which needs to be removed by additional heat treatment. In addition, leaching of Si from rice husk ash usually requires a fusion method at high temperature (above 500°C) because some of the Si content has turned into crystalline Silica after combustion. Another drawback of the conventional procedures lies in the focus of utilization.

Most previous research focused on advanced material with high capability, and most of the time utilize severe conditions (high temperature and pressure) which dictates the use of sophisticated apparatuses. Meanwhile, rice husk is mostly produced in rural area where those kinds of sophisticated apparatuses are rare or not exist. Therefore, while it is good to utilize rice husk for advance material, from the point of view of feasibility, the development of a procedure to utilize rice husk that can be easily done in the rural area need to be explored.

This paper addresses these drawbacks by developing a procedure with the lean condition and use simple equipment to utilize rice husk as a zeolite precursor, which will promote the utilization of rice husk directly in a rural area. Two of the above-mentioned drawbacks of the conventional procedure will be addressed as follows: (1) The problem of Si recovery method will be addressed by the application of direct Si leaching from rice husk. Si in rice husk exists as amorphous silica, and amorphous silica can react with an alkali solution to produce water-soluble alkali silicate, therefore, it is possible to recover Si from rice husk using alkali solution. This method could solve some of the problems posed by the conventional method, in which it does not cause air pollution and the carbon content can still be utilized for other purposes such as biomass fuel or chemical feedstock after the Si recovery process. Moreover, since the process does not need combustion, the energy requirement will be lower than the conventional method. (2) The problem of severe zeolite synthesis condition which requires sophisticated apparatuses will be addressed by developing a synthesis method at moderate temperature and atmospheric pressure, in which relatively low-cost equipment can be used. This research will combine both approaches and evaluate the synthesized zeolite produced by applying the procedure. It is expected that the development of a simple method of rice husk utilization as a zeolite precursor will promote the utilization of rice husk waste and thus also contribute to the waste management effort in rural areas.

2. RESEARCH METHODOLOGY

2.1. Material

The rice husk used in this experiment was obtained from Kanagawa Prefecture, Japan. Rice husk was washed with water to remove dirt and dried overnight before usage. No additional pretreatment was done. To study the property of rice husk, thermal analysis was done using Thermogravimetry-Differential Thermal Analysis (TG-DTA, Thermoplus TG8120, Rigaku Corporation), with the main purpose to determine the carbon content of rice husk (analysis condition: maximum temperature: 800°C; heating rate: 10°C/min; atmosphere: airflow). The ash of rice husk was analyzed using Inductively Coupled Plasma-Atomic Absorption Spectroscopy (ICP-AES, SPS7800, Seiko Instrument Inc.) after the first being digested by hydrofluoric acid, to determine the ash chemical composition.

2.2. Si Recovery Experiment

Si recovery experiment was performed at room temperature and atmospheric pressure using sodium hydroxide (NaOH) solution (Wako Pure Chemical Industries Ltd.). For each experiment, 2 g of rice husk and 4 mL of sodium hydroxide solution were mixed in a Teflon beaker using a magnetic stirrer at 400 rpm. The influence of sodium hydroxide concentration, recovery time, and rice husk particle size on recovered Si amount was investigated by varying those parameters. Rice husk samples with various sizes were prepared by milling with a food blender for 20 seconds, followed by sieving them into the desired particle size. The recovered Si amount was measured by analyzing the filtrate of NaOH solution obtained from each recovery experiment using ICP-AES. The optimum condition for silica recovery determined in this stage would be used to prepared sodium silicate solution for the zeolite synthesis step. To confirm the usability of recovered Si by the proposed method, zeolite A (LTA) was synthesized using a hydrothermal method and the result was compared to standard. The selection of zeolite A is based on its easy synthesis, and also its wide application in the detergent industry. The comparison of both Si recovery method is shown in **Figure 1**.

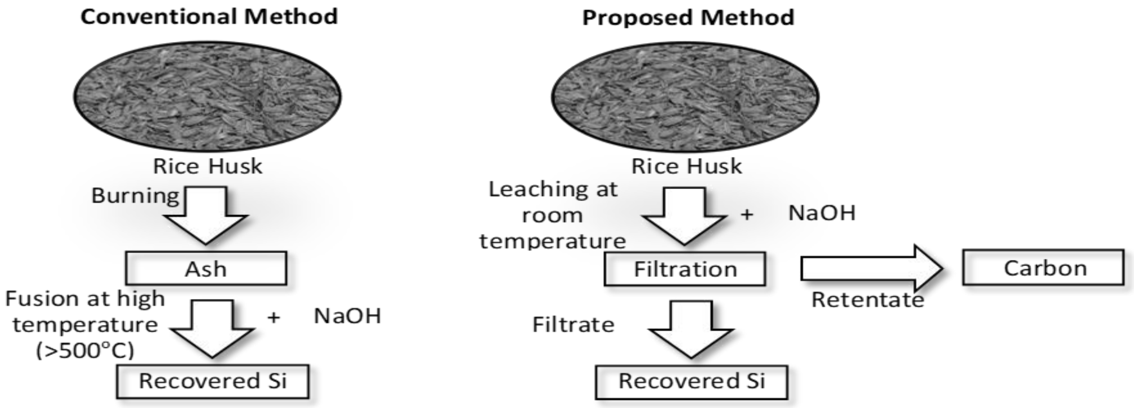

Figure 1. Comparison of conventional method and proposed method for Si recovery from rice husk.

2.3. Zeolite Synthesis

Zeolite synthesis was performed at moderate conditions (open beaker synthesis at moderate temperature and atmospheric pressure). Si recovered from the previous step (in the form of sodium silicate solution) was used as Si source, sodium aluminate (Wako Pure Chemical Industries Ltd.) was used as Al source, and NaOH (Wako Pure Chemical Industries Ltd.) was used as a mineralizer. Sodium silicate solution, sodium aluminate, and sodium hydroxide were mixed at Si to Al ratio of 2 to 1 mol ratio (1 N of NaOH was added with a ratio of 1 to 1 to sodium silicate solution). The mixture was mixed for 30 minutes, followed by hydrothermal treatment at 90°C and atmospheric pressure. This study only evaluates the influence of time on the final products. After synthesis, the suspension was filtered to separate the solid from liquid, and subsequently the solid was washed using deionized water until the pH of washing water was between 6 to 8. This washing step aimed to remove residual NaOH and other water-soluble impurities. The solid product was then dried in an oven at 100°C. Characterization of the product was done using X-ray Diffraction Spectrophotometry (XRD, MultiFlex X-Ray Diffractometer, Rigaku Corporation) which is used to determine the crystallinity of the samples and Scanning Electron Microscopy (SEM, JSM-5310LV, JEOL Ltd.) which is used to study the morphology of the samples. XRD analysis was done using Cu as the source, and spectra were taken for 2θ value between 5° and 55°. To evaluate the ion exchange capacity of the synthesized zeolites, samples were subjected to a cation exchange capacity test (Sodium Acetate method, sodium concentration was analyzed using ICP-AES).

3. RESULT AND DISCUSSION

3.1. Analysis of Rice Husk and Rice Husk Ash

TG-DTA analysis of rice husk is shown in **Figure 2**. There are three weight loss observed in the curves: loss at a temperature range of room temperature to 100°C, loss at a temperature range of 250°C to 360°C, and loss at a temperature range of 360°C to 480°C. The first weight loss is attributable to the release of gases and water vapor, and it was confirmed by the weak endothermic DTA peak observed at that temperature range.

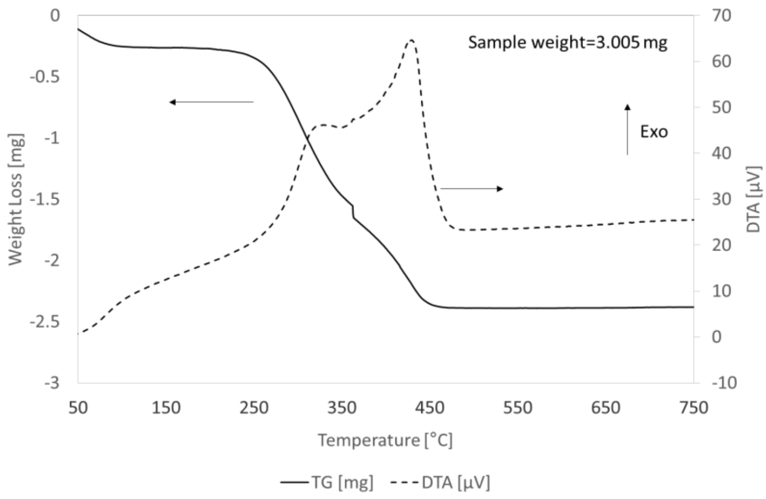

Figure 2. TG-DTA curve of rice husk

The second weight loss is attributable to the release and oxidation of volatile organic content of rice husk, as supported by the presence of exothermic DTA peak due to the oxidation. The exothermic peak was not high, because some of the heat produced by oxidation of carbon was used to evaporate the volatile content. The third peak is attributable to the oxidation of carbon content, and this weight loss was accompanied by a strong exothermic DTA peak that originated from the oxidation heat of carbon. From the weight loss calculation of the TG-DTA result, it can be determined that the carbon content of rice husk was 70.54% (the calculation only considered the weight loss due to oxidation of volatile organic compound and carbon), and the gas and water content was 8.44%.

The chemical composition of rice husk ash obtained using ICP-AES is presented in **Table 1**. The major constituent of rice husk ash was Si, accompanied by minor content of magnesium, iron, manganese, titanium, and calcium. The major part of the remaining component (36.80%) was oxygen because the rice husk ash was prepared by combustion under airflow, and most of the elements exist in their oxide form. Al was not detected in the sample, therefore to supply Al for zeolite synthesis, the addition of Al source is necessary. Sodium aluminate was used in this experiment.

The Si content of the rice husk may vary based on a variety of paddy. However, the value is usually above 15% (Singh, 2018), therefore it is feasible to use rice husk as Si source.

Table 1. Chemical composition of rice husk ash obtained by ICP-AES

Element	Content [wt.%]
Si	61.9
Mg	0.3
Fe	0.2
Mn	0.1
Ti	0.3
Ca	0.4
Other	36.8

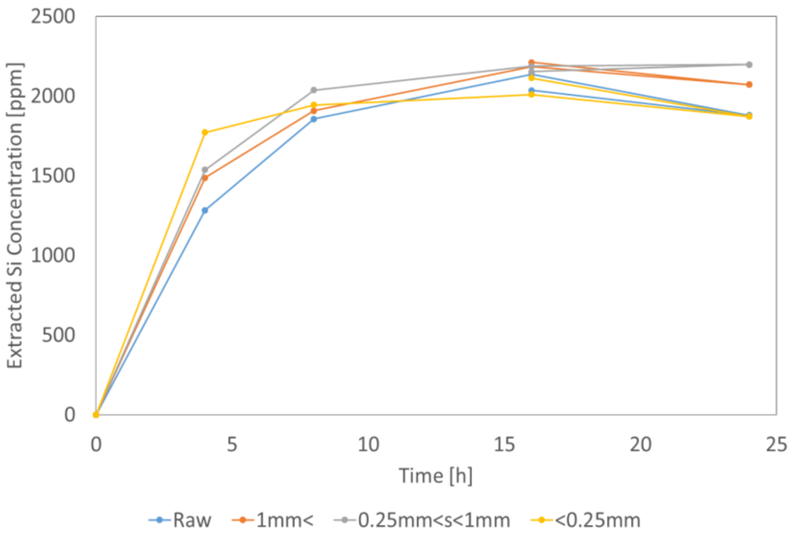

Figure 3. Influence of particle size and recovery time to the recovered amount of Si (NaOH concentration: 0.1 N)

3.2. Silicon Recovery

The result from the silicon recovery experiment using 0.1 N of NaOH is shown in **Figure 3**. It can be observed that the particle size of rice husk did not influence the silicon recovery result, as the variation in particle size did not significantly influence the results. In the early stage of the recovery, rice husk with the smallest particle size (smaller than 0.25 mm) showed a higher Si recovery amount compared to another particle size. However, as the recovery progress and reach saturation, it was observed that the recovery result was not influenced by the particle size. Moreover, the figure also showed that the recovery reached saturation after 16 hours for all particle size, thus this time can be considered as optimum recovery time.

Figure 4 shows the influence of NaOH concentration on the Si recovery amount. The experimental value is displayed in a blue line with a closed circle marker. It can be observed that Si recovery amount increase with the increase of NaOH concentration up to NaOH concentration of 1 N, after which Si recovery amount did not change significantly. Comparing this result to the theoretically recoverable Si at a specific concentration of NaOH (assuming that the concentration of Si in rice husk unlimited) which is shown by the orange line; it can be seen that at low NaOH concentration, the experimental value is close to that of the theoretical value. However, as NaOH concentration increase, the experimental value started to reach saturation and the difference between the experimental value and theoretical value become wider. This can be due to the fact that NaOH also reacts with other rice husk constituents, which reduce its reaction and effectivity for Si recovery, as well as due to the existence of unrecoverable Si fraction in rice husk. It is known that NaOH reacts with lignin, therefore it was considered that some of NaOH were consumed for this reaction.

By comparing the experimental value with the total content of Si in rice husk shown by the grey dash line, it can be seen that the experimental value start to reach saturation after 65% of Si in rice husk has been recovered, and did not increase significantly with a further increase of NaOH concentration.

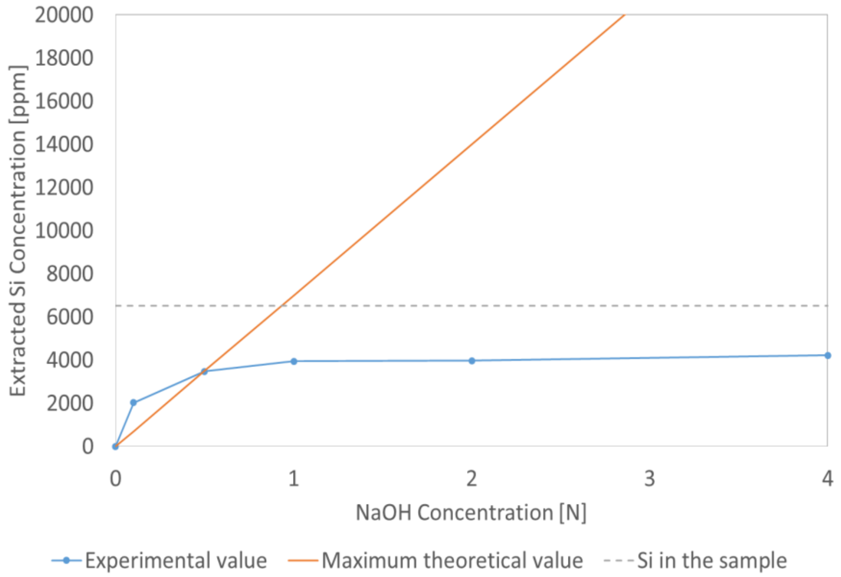

Figure 4. Comparison of experimental results and theoretical value recovered Si

This result supports the hypothesis that there are unrecoverable Si fraction in rice husk, since the increase of NaOH concentration cannot increase Si recovery amount further. This unrecoverable Si fraction is thought to be caused by the presence of lignocellulosic material that covers Si in rice husk, thus rendering it inaccessible for reaction with NaOH.

Table 2 presents the comparison of the Si recovery method using the conventional method (fusion method) and the proposed method. It can be seen that the proposed method showed a comparable result to the conventional method regardless of the lower temperature and chemical requirement. This could result in less cost and low environmental impact of the proposed method, which proved the superiority of this method.

To confirm the usability of Si recovered using the proposed method, the Si recovered in the form of sodium silicate solution was used to synthesize zeolite A (LTA). The analysis of the product in the form of XRD spectra and SEM images is shown in **Figure 5**. XRD spectra showed zeolite A spectra with good crystallinity. Furthermore, the cubic shaped particles could be observed from the SEM image, which further supports the result of zeolite A synthesis. This analysis result proved that Si recovered with the proposed method can be utilized as zeolite precursor.

Table 2 Comparison between Si recovery using conventional method and the proposed method

	Conventional Method (Fusion Method)	**Proposed Method**
	Condition	
Temperature	550°C	Room temperature
Amount of NaOH	2.4 g of NaOH per 1.2 g Si content	0.48 g of NaOH per 1.2 g Si content
	Result	
Extracted Si	68%	65%

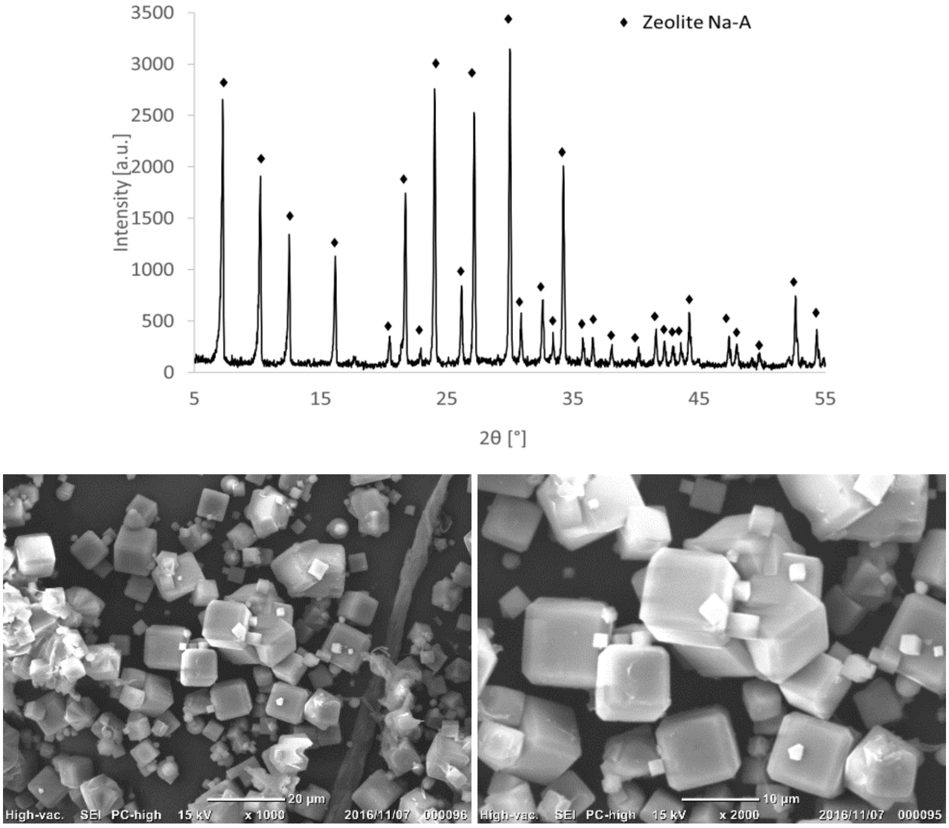

Figure 5. XRD (top) and SEM (bottom) of zeolite A synthesized using recovered Si (Synthesized using the hydrothermal method at 120°C with Si to Al ratio of 1:1)

3.3. Synthesis of Zeolite at Moderate Condition

Synthesis of zeolite at moderate condition was performed at 90°C and atmospheric pressure. The reason for this selection is that 90°C is high enough to make the synthesis proceed faster while still low enough to be achieved with simple apparatus. Studies reported that zeolite can be performed using hydrothermal process at lower temperature. However, it takes several days to achieve the full synthesis (Belviso et al., 2015; Hikichi et al., 1985). On the other hand, atmospheric pressure can be easily achieved using an open vessel system.

In this work, zeolite synthesis was performed using an open beaker system. The ratio of Si to Al was fixed to 2 to 1, and the influence of synthesis time was studied. XRD analysis result is shown in **Figure 6**. It can be observed that given enough synthesis time, zeolites could be synthesized from rice husk at moderate temperature and atmospheric pressure. Synthesis time of 3 hours produced only cristobalite (crystalline silica) without any formation of zeolites. A broad background peak was also observed due to the presence of an amorphous phase. From this result, it can be concluded that 3 hours was not enough for zeolite synthesis. An increase in treatment temperature to 6 hours resulted in the dissolution of cristobalite and formation of zeolite X (FAU) and a small amount of zeolite P (GIS).

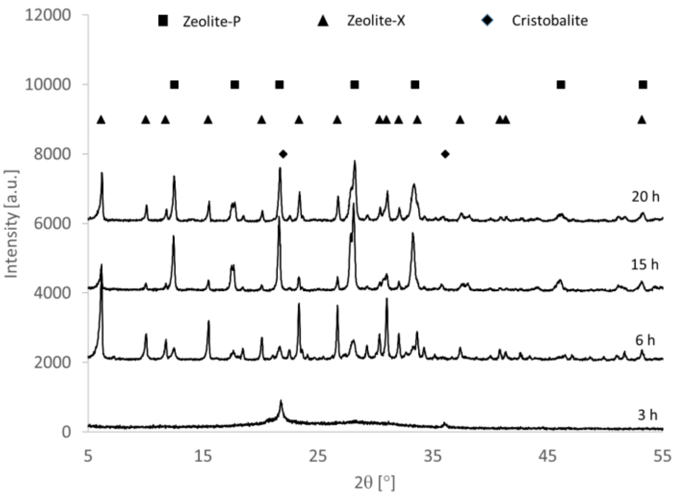

Figure 6. XRD spectra of sample synthesized at various time

Furthermore, when the treatment time was increased to 15 hours, the amount of zeolite P produced increased and the amount of zeolite X decreased, and zeolite P became the major constituent. It was thought that with time progress, zeolite X was converted to zeolite P. When the treatment time was further increased to 20 hours, the major constituent of the product was still zeolite P. However, based on the XRD peak intensity of the products, zeolite P composition decreased and zeolite X composition increased compared to the product of 15 hours. The decrease in the solution volume due to evaporation was significant at this point of time. Therefore, the reverse in trend in which zeolite P decompose and zeolite X being formed again was thought to be caused by this decrease in volume and increase in the concentration of a solution resulting from it.

Selected SEM images of the samples are shown in **Figure 7**. It can be seen that after the synthesis process, Si from rice husk was transformed into zeolite particles. The particle size of both zeolite X (3 hours synthesis and zeolite P (15 hours synthesis) were around 2 µm, with the particle size of 3 hours product was slightly bigger than that of 15 hours product. The reduction in particle size between the synthesis time of 6 and 15 hours was due to the decomposition of zeolite X before it is converted to zeolite P.

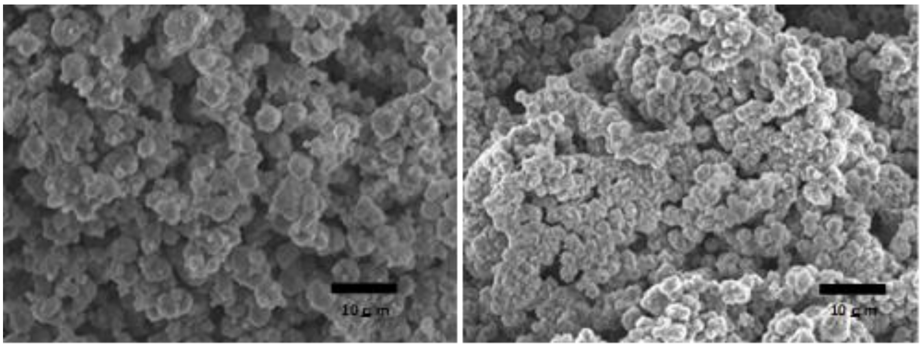

Figure 7. SEM images of selected samples: Zeolite synthesized by 6 hours of hydrothermal treatment (left), Zeolite synthesized by 15 hours of hydrothermal treatment (right)

Table 3 Cation Exchange Capacity of selected samples

Sample's Treatment Time [h]	Main Constituent	Cation Exchange Capacity [meq/100 g]
6	Zeolite X	361
15	Zeolite P	457
20	Zeolite P	430

3.4. Cation Exchange Capacity Measurement Results

It has been observed that instead of zeolite A, zeolite X and P were formed at a lean synthesis condition. Because the main purpose of this research is to provide rice husk utilization method focused in a rural area, it is then necessary to investigate whether zeolite X and P can be used in a rural area. The intended application of zeolite X and P in a rural area is for water purification, therefore, their cation exchange capacity (CEC) need to be evaluated.

The results of the CEC measurement of selected samples are shown in **Table 3**. Samples containing zeolite P as a major component showed a higher CEC compared to the samples containing zeolite X as a major component, which means that zeolite P possessed a higher cation exchange capacity compared to zeolite X. Comparison of sample synthesized for 15 hours and 20 hours showed that the 15 hours sample possesses a higher CEC compared to 20 hours sample, despite the fact that both samples' major component was zeolite P. This was because the 20 hours sample has lower zeolite P content compared to 15 hours sample, as shown by the intensity of XRD pattern (**Figure 6**). The lower content of zeolite P resulted in the lower cation exchange capacity and this further supports the conclusion of the high cation exchange capacity of zeolite P.

From the result above, it can be concluded that the synthesis of zeolite at moderate condition using Si from rice husk could produce zeolite with good CEC value, thus have a high potentiality to be used as water purification material.

4. CONCLUSION

Recovery of Si from rice husk was successfully performed using sodium hydroxide solution. It was found that the particle size of rice husk did not influence the maximum Si recovery amount. On the other hand, recovery time and sodium hydroxide concentration increased the recovery amount until it reached saturation. The optimum condition for Si recovery using sodium hydroxide was a recovery time of 16 hours and sodium hydroxide concentration of 1 N.

The usability of recovered Si was proved by application as precursors of zeolite A. Furthermore, zeolites were successfully synthesized from recovered Si using moderate temperature and atmospheric pressure. Synthesis for 6 hours resulted in a product that mainly composed of zeolite X, while a longer time up to 15 hours resulted in a product that mainly composed of zeolite P. The procedure to recover Si presented in this paper uses simple equipment to utilize rice husk as a zeolite precursor, which will promote the utilization of rice husk directly in a rural area.

Among zeolites synthesized in this experiment, sample prepared by synthesis time of 15 hours (major component: zeolite P) showed the highest CEC, which makes it a promising material to be used as water purification material which will be very useful in rural area.

REFERENCES

Belviso, C., Giannossa, L. C., Huertas, F. J., Lettino, A., Mangone, A., & Fiore, S. (2015). Synthesis of zeolites at low temperatures in fly ash-kaolinite mixtures. *Microporous and Mesoporous Materials*, *212*. https://doi.org/10.1016/j.micromeso.2015.03.012

Carmona, V. B., Oliveira, R. M., Silva, W. T. L., Mattoso, L. H. C., & Marconcini, J. M. (2013). Nanosilica from rice husk: Extraction and characterization. *Industrial Crops and Products*, *43*(1). https://doi.org/10.1016/j.indcrop.2012.06.050

Dey, K. P., Ghosh, S., & Naskar, M. K. (2012). A facile synthesis of ZSM-11 zeolite particles using rice husk ash as silica source. *Materials Letters*, *87*. https://doi.org/10.1016/j.matlet.2012.07.079

Ding, L., Zou, B., Shen, L., Zhao, C., Wang, Z., Guo, Y., Wang, X., & Liu, Y. (2014). A simple route for consecutive production of activated carbon and liquid compound fertilizer from rice husk. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *446*. https://doi.org/10.1016/j.colsurfa.2014.01.055

Food and Agricultural Organization of the United Nations. (2017). *Rice Market Monitor*.

Hikichi, Y., Hukuo, K. iti, & Miwa, T. (1985). LOW TEMPERATURE SYNTHESIS OF FAUJASITE-TYPE ZEOLITE FROM CRISTOBALITE ROCK. *Yogyo Kyokai Shi/Journal of the Ceramic Society of Japan*, *93*(11). https://doi.org/10.2109/jcersj1950.93.1083_717

Mohamed, R. M., Mkhalid, I. A., & Barakat, M. A. (2015). Rice husk ash as a renewable source for the production of zeolite NaY and its characterization. *Arabian Journal of Chemistry*, *8*(1). https://doi.org/10.1016/j.arabjc.2012.12.013

Prasetyoko, D., Ramli, Z., Endud, S., Hamdan, H., & Sulikowski, B. (2006). Conversion of rice husk ash to zeolite beta. *Waste Management*, *26*(10). https://doi.org/10.1016/j.wasman.2005.09.009

Purnomo, C. W., Salim, C., & Hinode, H. (2012). Synthesis of pure Na-X and Na-A zeolite from bagasse fly ash. *Microporous and Mesoporous Materials*, *162*. https://doi.org/10.1016/j.micromeso.2012.06.007

Santasnachok, C., Kurniawan, W., & Hinode, H. (2015). The use of synthesized zeolites from power plant rice husk ash obtained from Thailand as adsorbent for cadmium contamination removal from zinc mining. *Journal of Environmental Chemical Engineering*, *3*(3). https://doi.org/10.1016/j.jece.2015.07.016

Singh, B. (2018). Rice Husk Ash. In *Waste and Supplementary Cementitious Materials in Concrete*. Woodhead Publishing.

Soltani, N., Bahrami, A., Pech-Canul, M. I., & González, L. A. (2015). Review on the physicochemical treatments of rice husk for production of advanced materials. In *Chemical Engineering Journal* (Vol. 264). https://doi.org/10.1016/j.cej.2014.11.056

United States Department of Agriculture. (2019). *Indonesia Rice: Area Reduced due to Corn Expansion. Commodity Intelligence Report.*