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Synthesis of Type A Zeolite from Rice Husk Ash and Its Application as a Builder on Effervescent Tablet Form Detergent

The application of phosphate compounds as a builder in a detergent formulation created eutrophication that encouraged industry to produce more eco-friendly detergents. To overcome that problem, phosphate can be substituted by zeolit that is more effective in cleaning and also biodegradable. In this study, zeolite was synthesized from rice husk ash using a melting method followed by hydrothermal processes. Effervescent detergent tablets were prepared with the following formulations: 3 formulations containing zeolite (F1–F3), 3 formulations containing sodium tripolyphosphate (STPP: P1–P3) and 1 control formulation. The synthesized zeolit was analysed by XRD (X-Ray Diffraction), FTIR (Fourier-Transform Infrared Spectroscopy), SEM (Scanning Electron Microscopy) and cation exchange capacity (CEC). Furthermore, all detergent formulas were characterized for flowability, compressibility, compatibility, disintegration time, pH, cleaning action and biodegradability. The results of FTIR, XRD and SEM characterization showed that the synthesized zeolite was an amorphous type-A crystal and the predominance of the amorphous phase with a cubic structure and CEC value of 95.71 $cmol^{(+)}\ kg^{-1}$. In this study the formulation F1 with 15 % zeolite was found to be the best formulation with granule flow rate parameters of 13.6 g/s, stationary angle of 22.0°, compressibility of 16.6 %, detergent tablet hardness accounted to 0.81 kgf/cm^2, crushed time of tablet detergent of 1.5 min, pH 6.7, and biodegradability value of 70.3 % in BOD_5 test. A higher concentration of zeolite provided a better cleaning effect of the detergent tablets.

Keywords: Builder, zeolite, rice husk ash, detergent, effervescent tablet form

Synthese von Zeolith A aus Reisschalenasche und seine Anwendung als Builder in Waschmitteltabs. Der Einsatz von Phosphatverbindungen als Builder in Waschmittelformulierungen führte zu einer Eutrophierung, die die Industrie zur Herstellung umweltfreundlicherer Waschmittel veranlasste. Um dieses Problem zu überwinden, kann Phosphat durch Zeolith ersetzt werden, das wirksamer in der Reinigung und auch biologisch abbaubar ist. In dieser Studie wurde Zeolith aus Reishülsenasche mit Hilfe einer Schmelzmethode synthetisiert, gefolgt von hydrothermalen Prozessen. Es wurden Waschmittelbrausetabletten mit folgenden Formulierungen hergestellt: 3 Zeolithhaltige Formulierungen (F1–F3), 3 Formulierungen mit Natriumtripolyphosphat (STPP; P1–P3) und 1 Kontrollformulierung. Der synthetisierte Zeolith wurde mittels XRD (Röntgenbeugung), FTIR (Fourier-Transformations-Infrarotspektroskopie), SEM (Rasterelektronenmikroskopie) und der Kationenaustauschkapazität (CEC) analysiert. Des Weiteren wurden alle Waschmittelformulierungen hinsichtlich Fließfähigkeit, Kompressibilität, Verträglichkeit, Zerfallszeit, pH-Wert, Reinigungswirkung und biologischer Abbaubarkeit charakterisiert. Die Ergebnisse der FTIR-, XRD- und SEM-Charakterisierung zeigten, dass es sich bei dem synthetisierten Zeolith um einen amorphen Typ-A-Kristall handelt und dass die amorphe Phase mit einer kubischen Struktur und einem CEC-Wert von 95,71 $cmol^{(+)}\ kg^{-1}$ überwiegt. Die Formulierung F1 mit 15 % Zeolith war mit einem Granulatfluß von 13,6 Gramm/Sekunde, einem stationären Winkel von 22,0°, einer Kompressibilität von 16,6 %, einer Tablettenhärte von 0,81 kgf/cm^2, einer Tablettenzerfallszeit von 1,5 Minuten, einem pH-Wert von 6,7 und einer biologischen Abbaubarkeit von 70,3 % im BOD_5-Test die beste Formulierung dieser Untersuchung. Eine höhere Konzentration von Zeolith lieferte eine bessere Reinigungswirkung der Waschmittelmitteltabletten.

Stichwörter: Builder, Zeolith, Reisschalenasche, Waschmittel, Waschmittelbrausetabs

1 Introduction

Detergents are compounds that are used as cleaning agents to remove dirt or other foreign matter from material surfaces and they became part of every household in the world. Detergent production in Indonesia is mostly in powder form, cream, and liquid detergents. In this study, compact or tablet form detergent was chosen based on performance and price considerations. In addition, eco-friendly detergents must be considered to minimize environmental impacts.

Detergents in tablet form should disintegrate and dissolve immediately upon contact with water. However, the compact or solid form makes a detergent difficult to disintegrate, in order to overcome this the effervescent system is applied to the detergent formula [1]. The effervescent system can improve the dispersibility of tablet detergent and for that purpose a combination of citric acid and bicarbonate is used in this study [2].

Generally, a detergent tablet consists of 4 %–30 % surfactants; 5 %–60 % builders which usually are phosphate, citrate, acetate, or silicate (zeolite) compounds; fillers, and further additives such as fragrances, dyes and bleach [3]. Builders increase the washing efficiency of surfactants by deactivating water hardness-causing minerals (Ca^{2+} and Mg^{2+} ions) [4]. The addition of phosphate as a builder in detergents has been reported to have a significant consequence on the ecosystem [5]. Phosphate deposited in water may result in eutrophication. Eutrophication is a phenomenon of water enrichment by plant nutrients.

When the concentration of nutrients in the water increases, there will be more plant growth. As a consequence, the dissolved oxygen in the water became saturated which causes a lack of oxygen in the bottom of the water (hypolimnion). Also, there will be an explosion of *cyanophyta* that causes problems with taste and odor in the water. Then, the water may no longer be edible, fish populations decline, and aquatic weeds growth could disrupt the functionality of the waters [6].

According to Global Market Insights Inc. [7], zeolite 4A is the most preferred type of builder in the global market industry for detergent tablet production. Zeolite 4A is a synthetic zeolite that belongs to the zeolite type with the framework of LTA (Linde Type A) [8]. Zeolite is biodegradable and safe for the environment that can replace the role of phosphate as a builder in detergents [9] and is a mineral consisting of alumina, silica, and oxygen [10]. Previous studies reported, zeolites synthesized from rice husk ash can be formulated into builders in detergent manufacturing [11].

Rice husk is an abundant byproduct of rice milling. The most dominant element identified in rice husk is silica (Si). The silica content in rice husk ash reaches 89% [12] making it a potential source for the production of synthetic zeolite. Zeolite synthesized from rice husk ash can be a type-A with a high selective ability to adsorb Ca^{2+} and Mg^{2+} ions [13].

Zeolites possess poor flow properties, so a granulation method for manufacturing is needed to overcome the problem. Wet granulation is one of the common methods used for tablet detergent production [14]. In this study seven detergent tablet formulations were investigated; formulations F1, F2 and F3 contained 15%, 20% and 25% respectively of rice husk ash zeolite. In addition, three formulations containing STPP as a builder (formulations P1, P2 and P3) in the same concentration as the zeolite formulations and one formulation without a builder were included for comparison. This is particularly useful to investigate the optimal concentration of zeolite as a builder in detergent tablets and to determine the efficacy compared to the known builder. The detailed composition of the detergent tables is displayed in Table 1.

The objective of our work was to develop detergent formulations in tablet form that contain type-A zeolite as a builder that was synthesized from rice husk ash to produce a more ecological detergent.

2 Materials and Methods

2.1 Materials

The materials used were rice husk obtained from agricultural areas in the sub district of Sigi Biromaru, Sigi Regency, Central Sulawesi. Other materials as ingredients for synthesis, formulation and evaluation were: Hydrochloric acid 37% (Emsure, ACS, ISO, Reag. Ph Eur, MERCK, Germany), sodium hydroxide (Emsure, ISO, Reag. Ph Eur, MERCK, Germany), anhydrous aluminium oxide (MERCK, Germany), sodium lauryl sulfate (SLS, Hawwari Trading Apriansyah, Bogor, Indonesia), sodium tripolyphosphate (STPP granula, Fengbao, China), polyvinylpyrrolidone (PVP K-30, MERCK, Germany), citric acid monohydrate (Emsure, ACS, ISO, Reag. Ph Eur, MERCK, Germany), tartaric acid (Emsure, ACS, ISO, Reag. Ph Eur, MERCK, Germany), sodium hydrogen carbonate (Emsure, ACS, Reag. Ph Eur, MERCK, Germany), sodium chloride (Emsure, ACS, ISO, Reag. Ph Eur, MERCK, Germany), and distilled water (Water One OneMed).

2.2 Methods

2.2.1 Rice husk ash preparation

Rice husk was washed using distilled water, and dried subsequently. Rice husk was mashed, ignited in the furnace at 700 °C for 6 h. 5 grams husk ash was mixed with 10% HCl solution in a beaker (ratio, 1:25). The beaker was placed on a hot plate at 100 °C–110 °C, and intensely stirred for 1 hour. Finally the rice husk ash was filtered, rinsed with distilled water and dried at 100 °C for 24 h [15].

2.2.2 Melting of rice husk ash and extraction of Si and Al

The method was performed according to Kurniawan [16] with slight modification. 5 grams rice husk ash were mixed with NaOH (ratio, 1:1). The mixture was ground in a stainless steel crucible. Then, the mixture was melted at 750 °C for 1 hour in the kiln. Subsequently, the mixture was suspended in 100 ml distilled water (10 ml/g) and transferred to a polyethylene bottle for aging about 24 h at room temperature. The supernatant as a source of Si and Al was extracted by filtration of the solution.

2.2.3 Zeolite A synthesis

The extract (relative molar ratio of 3,165 $Na_2O : Al_2O_3$: 1,926 SiO_2 : 128 H_2O) was slurried by adding 6 grams NaOH and 8.5 grams Al_2O_3 to regulate the molar ratio Si/Al = 1 suitable for the synthesis of zeolite-A [10]. The hydrothermal crystallization was conducted for 12 h in the oven at 100 °C. After the hydrothermal treatment, the residual solid was separated from the filtrate, washed with distilled water until the pH was 9–10 and dried for 12 h at 100 °C. Then, the product was stored for further characterization [17].

Component	Concentration of formula (wt%)						
	F1	F2	F3	P1	P2	P3	Control
Zeolit-A	15	20	25	–	–	–	–
Sodium lauryl sulfate	15	15	15	15	15	15	15
Citric acid	10	10	10	10	10	10	10
Tartrat acid	18	18	18	18	18	18	18
Sodium bicarbonate	30	30	30	30	30	30	30
Sodium tripolyphosphate	–	–	–	15	20	25	–
Polyvinyl alcohol	2	2	2	2	2	2	2
Sodium chloride	ad 100	ad 100	ad 100	ad 100	ad 100	ad 100	ad 100

Note: F1.F2.F3: Formula 1.2.3; P1.P2.P3: comparison 1.2.3; The weight of each tablet is 3 gram.

Table 1 Composition of tablets detergent

2.2.4 Characterization of zeolite

- *X-Ray Diffraction (XRD) pattern:* XRD pattern was carried out using x-ray diffraction (*Shimadzu 7000*) method with 40 kV voltage, 30 mA current, 2θ angle of 0–50 (deg) and scan speed of 0.02 deg/s [15].
- *Fourier Transform Infrared (FT-IR) spectra*: FT-IR (*Shimadzu Irprestige-21*) characterization was carried out on zeolite-A sample in the range of 4000 cm^{-1} ~ 400 cm^{-1} using 0.5 mg powder samples mixed with 250 mg KBr [18].
- *Morphology.* Morphology was observed by using Scanning Electron Microscopy (SEM, *JEOL-JSM-6510LA*). Samples were placed on gold coating machines and characterized on SEM instruments with a voltage of 15 kV at 5 000 × and 10 000 × magnification [15].
- *Cation Exchange Capacity (CEC).* CEC was determined by dispersing 0.5 g zeolite A in 500 mL of 0.005 mol/L $CaCl_2$ solution for 30 min with continuous stirring (400 rpm) at room temperature, then the sample is filtered and the residual Ca^{2+} concentration is measured by titration with EDTA [18].

2.2.5 Formulation of tablet detergent

Wet granulation method was carried out for all formulations. Citric acid, tartrate acid, zeolite, SLS 6.5 % (inner phase) were mixed for 10 min. Some PVP was dissolved in ethanol and added to the mixture until a wet mass was formed. This wet mass was passed through sieve no. mesh 20 and the granules were dried in an oven at 54 °C for 18 hours (acid component). In other containers, sodium bicarbonate, NaCl, 6.5 % SLS (part of the inner phase) and the remaining of PVP which had been dissolved in ethanol was mixed until a wet mass was formed. Then the wet mass was sieved with a mesh sieve no. 20 to produce granules. The granules were dried in an oven at 54 °C for 18 hours (base component). Furthermore, the dry mass (acid component and base component) was added to the remaining of SLS 2 % (outer phase) as lubricant. Evaluation of granule quality includes flow and compressibility properties. The granule mixture was compressed using conventional tablet printing presses at a pressure of ± (0.025–0.3) MPa (based on the results of the conversion value of detergent tablet tensile strength) [21]. The tablets were dried in an oven at 54 °C for 90 min, then wrapped in aluminum foil and packaged in a plastic tube for further evaluation of the tablet quality including compressibility, hardness, disintegration time, pH, detergency power and biodegradability. The same work was done for each formula and carried out at room temperature < 23 °C and a relative humidity of 40 % [22].

2.2.6 Characterization of detergent in the tablet form

Flowability (Angle of repose)

The flowability was determined by using the fixed funnel method of Sun [23]. The used funnel has a top diameter of 10 cm, a cone height of 7.5 cm, a hole diameter below 1.0 cm and a mouth mouthpiece of 2.0 cm. Funnels are placed (10.5 ± 0.2) cm above the flat plane to the mouth of the lower funnel. The flow time is measured by means of a 25 g granule poured slowly into a funnel that is closed down. The funnel lid is opened, the granule is allowed to flow out. Time is recorded with a stopwatch until all granules flow out. Flow velocity is calculated in units of g/time.

Flow properties can also be determined by calculating the angle of repose employing granules falling from the measurement of flow time measured by the cone height formed and the length of the granule. The angle of repose calculated by:

$tan\ \alpha = h/r$
α: angle of repose
h: height
r: radius

Compressibility

50 grams granule was put in a 100 ml measuring cup, then the volume was measured (v_1). Bulk density = The mass in the measuring cup was taped 500 times from a height of 2.5 cm to a fixed volume (v_2) [24]. Then the bulk density (ρ_b) and density (ρ) were compressed, calculated by the equation:

$$\rho\ \text{bulk} = m/v_1 \text{ and } \rho\ \text{tapped} = m/v_2$$

Compressibility was calculated by equation:

$$\%\ \text{Compressibility} = \frac{\rho\ \text{tapped} - \rho\ \text{bulk}}{\rho\ \text{tapped}} \times 100\,\%$$

Bulk density: The type of granule that has not been compressed
Tapped density: The type of granule that has been compressed

Hardness

Tablet hardness was measured using a hardness tester (*Digital force gauge Model: EL-500*) by placing a tablet vertically between the pressure points on the tool. Pressure might be adjusted so that it was on a scale of 0. Subsequently, screws were rotated until the tablet fractures and the hardness of of the tablet was measured in kgf/cm^2 [24].

Disintegration time of detergent

1 gram of detergent was immersed into the 10 liters volume of distillated water at 25 °C. Disintegration time determined with a stopwatch started when detergent was immersed until no residues remained [1].

pH measurement

A pH meter was calibrated using buffers of pH 4, 7 and 10. Using the calibrated pH meter (*NeoMet Model pH-240L ISTEK*), 0.1 % solution of detergent of each formulation was measured and recorded [25].

Cleaning actions

2 gram of sauce and tea were applied to the cotton cloth and dried for ± 24 h. The cloth was soaked for 15 min in 200 mL of 0.1 % detergent solution and then stirred for 15 min at 4 rpm. The cloth was then rinsed with distilled water and dried. A few commercial powder detergents were used as comparing agents, namely commercial detergent A, commercial detergent B, and commercial detergent C. Control which was used was without stains, detergent, and builder [25].

Biodegradability test

Detergent biodegradability was measured through the 5-day biochemical oxygen demand (BOD_5) test. BOD_5 was conducted by preparing a detergent sample of 100 mg/L, stored in an incubator for five days at 20 °C. The amount of dissolved oxygen was measured after the first day and the fifth day using the Winkler titration method [25].

BOD = DO_0 – DO_5. The % BOD was calculated by equation:

$$\%' \text{ BOD} = \frac{\text{BOD}_{\text{Sample}} - \text{BOD}_{\text{Control}}}{\text{BOD}_{\text{Sample}}} \times 100\,\%$$

Statistical analysis

Data from zeolite characterization using XRD, FTIR, SEM, and CEC were analyzed descriptively. The results of the characterization of detergent include compressibility, hardness, disintegration time, pH value was analyzed using one-way ANOVA (Analysis of variants) in the SPSS 16.0 program. Biodegradability and cleaning action tests of detergent were analyzed descriptively.

3 Results and Discussion

3.1 Characteristics of zeolite synthesized from rice husk ash

3.1.1 X-Ray Diffraction pattern

The XRD pattern of zeolite synthesized from rice husk ash analysis by comparing the diffraction peaks with the Collection of Simulated XRD Powder Patterns for Zeolites [26] is shown in Fig. 1. In the diffractogram, peaks can be obtained

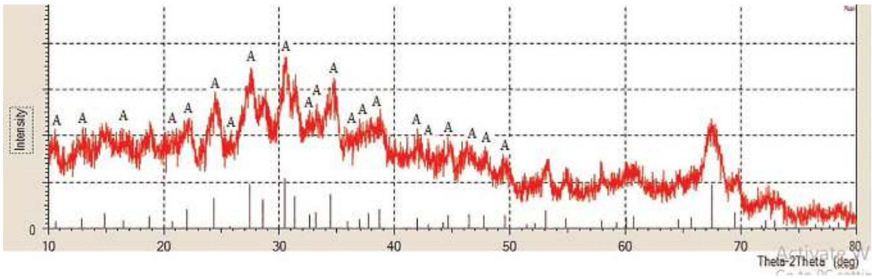


Figure 1 XRD diffractogram of zeolite synthesized from rice husk ash; remarks A: Zeolite A

Type A Zeolite from rice husk ash		Type A Zeolite from JCPDS Standard	
Angle 2θ (°)	d	Angle 2θ (°)	d
10.59	8.347	10.19	8.682
12.86	6.875	12.49	7.088
16.52	5.360	16.14	5.491
20.76	4.275	20.46	4.341
21.99	4.038	21.72	4.093
24.37	3.648	24.04	3.702
25.72	3.460	25.13	3.544
27.43	3.248	27.18	3.281
30.44	2.934	30.01	2.978
32.62	2.742	32.62	2.745
33.18	2.697	33.45	2.679
34.48	2.599	34.26	2.618
35.93	2.497	35.83	2.506
36.92	2.432	36.59	2.455
38.68	2.325	38.08	2.363
39.98	2.253	39.53	2.280
41.95	2.151	41.61	2.170
42.94	2.104	42.95	2.106
44.18	2.048	44.26	2.046
44.66	2.027	44.91	2.018
46.47	1.952	46.80	1.941
47.77	1.902	47.41	1.917
49.55	1.838	49.82	1.830

Source: Treacy and Higgins (2001)

Table 2 Comparison data of the type A zeolite from rice husk ash and standard JCPDS according to Bragg's law. The result of product was similar when the peaks of diffractogram or d value was similar with the zeolite standard. The comparison between zeolite A synthesized with standard JCPDS (Joint Committee on Powder Diffraction Standard) Linde Type A, Dehydrated (LTA) can be seen in Table 2.

Table 2 shows that the synthesized zeolite is a type A zeolite. Obtained by 23 peaks of zeolite A, these results indicate that the large number of peaks appeared, and the zeolite A formed has high purity [17]. The diffractogram pattern shows that the zeolite synthesized in this study has a crystalline phase mixed with an amorphous phase, mainly in the amorphous phase. The amorphous phase of zeolite was identified by the appearance of a diffractogram peak with high intensity in 2θ area around 5° until 35°. Sharp diffractogram peaks characterize the presence of the crystalline zeolite phase in the 2θ region ≥ 40.10° [26]. In this study, the high-intensity amorphous phase was seen at 2θ = 27.44° and 2θ = 30.44°.

3.1.2 FT-IR spectra

The results analysed by FT-IR are shown in Table 3 and Fig. 2. The absorption area of 1 250 – 950 cm^{-1} shows the presence of asymmetric stretching vibrations from Si–O and Al–O in the alumina silicate framework. The stretching symmetry of Si–O and Al–O appears in the absorption area around 820 cm^{-1} – 650 cm^{-1}. The bending vibration of Si–O and Al–O in the aluminosilicate framework of zeolites appears in the absorption area of around 500 cm^{-1} – 420 cm^{-1}. The presence of stretching vibrations and bending vibrations of Si–O and Al–O indicate that an aluminosilicate frame has been formed in the sample. One of the characteristics of zeolite is a double ring which is indicated by the appearance of absorption in the area of 650 cm^{-1} – 500 cm^{-1}. In the zeolite structure, there are internal links and external links. This double ring is an external link between the zeolite layers to one another [27]. The peaks indicated that the synthesized type A zeolite has the same criteria as the standard and the commercial products respectively.

3.1.3 SEM observation

The morphology of zeolite A determined by SEM is shown in Fig. 3. It has been reported that the initial ball-shaped morphology transformed to cubic-shaped grains or other crystal shapes after continuous dissolution and crystallizations. Such characteristic hollow structures of zeolitic minerals facilitate their application in several industrial processes and products. It was observed that the particles were mostly cubic. This result is similar to the study by Jha and Singh [10].

3.1.4 Cation Exchange Capacity

CEC is a measure of a cation exchanger which is usually expressed in 100 gram or $cmol^{(+)}\,kg^{-1}$ where 1 me/100 g = 1 $cmol^{(+)}\,kg^{-1}$. The zeolite cation exchange capacity is one

Zeolit Standard Wave Number/cm^{-1*}	Zeolit A synthesis results Wave Number/cm^{-1}	Zeolit A commercial Wave Number/cm^{-1***}	Interpretation*
420 – 300	374.19	378****	*Pore opening.* External
500 – 420	462.92	462	Bending Vibration O-T-O. Internal
650 – 500	559.36	553	*Double ring.* External
720 – 650	667.37	662	Symmetric Stretching Vibration. O-T-O. Internal
820 – 750	750.31	795	Symmetric Stretching Vibration O-T-O. Eksternal
1250 – 950	993.34	995****	Asymmetric Stretching Vibration O-T-O. Internal
1650 – 1600**	1647.21	1650	Bending Vibration H-O-H**
3600 – 3100**	3464.15	3450	Vibration O-H**

Note: (T=Si/Al) Sources: *Flanigen et al. (1974). **Socrates (1994). ***Gougazeh & Buhl (2014). ****Saraswati (2015).

Table 3 Interpretation of IR spectra of synthesized zeolite

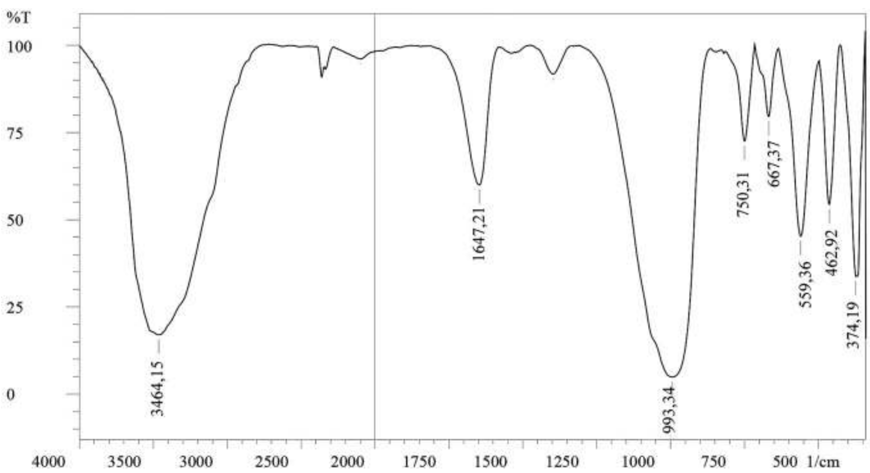


Figure 2 FTIR spectra of synthesized zeolite

of the factors that influence the detergency. Zeolite as a builder in the detergency process has the task of deactivating the water hardness ions, so that the surfactants are completely available for stain removal from the substrate. The results of CEC measurements showed that the synthesis value of zeolite A is 95.71 $cmol^{(+)}\ kg^{-1}$. Alfiansyah [11] obtained the optimum CEC value of zeolite-A which was applied as a builder in detergent was 80.80 $cmol^{(+)}\ kg^{-1}$ with detergency reaching 98 %. The CEC value is directly proportional to detergency. The higher the CEC value is, the higher of detergency ability.

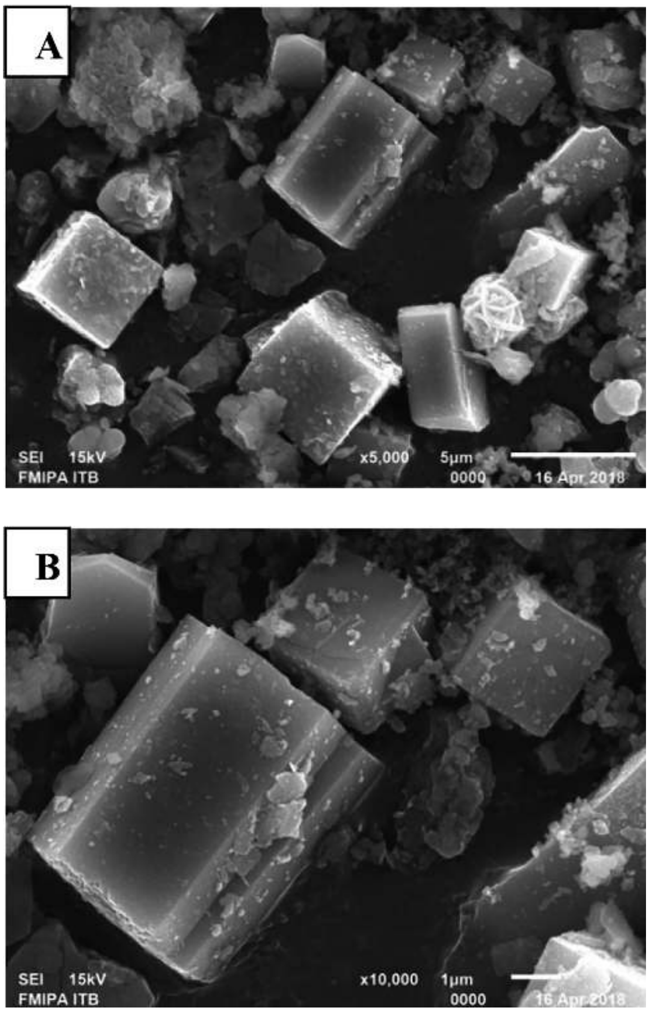


Figure 3 SEM photographs of synthesized zeolite (A; magnification: 1000 x; B; magnification: 5000 ×)

3.2 Characteristics of tablet detergent

Table 4 presents the properties of all detergent formulations (F1 to F3, P1 to P3) including the comparing and control formulations. A good granule flow rate is ≥ 10 g/s [28]. The results indicate that all formulas were found to have a good flow rate. Therefore, wet granulation process in detergent formulations with zeolite as a builder can improve the flow properties of zeolites which are known to have poor flow properties [14]. Based on the statistical analysis, it can be concluded that the lower the concentration of zeolite, the better of granule flow rate.

The flow properties were also calculated by using the angle of repose method. Based on literature, the angle of repose < 25° shows special flow properties and one of 25°–30° shows good flow properties [29]. The results indicate that the formulations F1–F3 and P1–P3 have special flow properties. Based on the statistics analysis, the difference in zeolite concentration does not significantly influence the granular angle value of the granule.

The compressibility results for all formulations show great compressibility properties. Based on the statistics analysis, it was shown that the lower the zeolite concentration used, the better the compressibility of the granule. Compressibility is the ability of the granule to decrease in volume under pressure. The smaller of compressibility value, the greater power flow from the granule [24].

Hardness is a parameter that describes durability of tablets in resisting mechanical stress, shock, and cracking of tablets during packaging, transportation, and distribution. The standard hardness of a detergent in the tablet form is between 0.25 and 3 kgf/cm^2. A pressure < 0.20 kgf/cm^2 is considered as fragile and is likely to cause damage to the detergent tablet during distribution. The hardness of 30 kPa (0.30 kgf/cm^2) is preferred because disintegration is more easily achieved [21]. The results of the all formulation are in accordance with the standard. Generally, the greater the pressure, the harder the tablet that is produced. Based on the statistics analysis, it was shown that the higher the concentration of zeolite used, the hardness of the tablet increased.

Disintegration time of all detergent tablets ranged from 1.5 to 6.04 min and the disintegration time of formulation F1 is the shortest. These results were found to be unacceptable with

Detergent	Flow rate/ $g\ s^{-1}$	Angle of Repose°	Compressibility Index/%	Hardness/ $kgf\ cm^{-2}$	Disintegration time/min	pH	BOD_5/%
F1	13.65 ± 0.41	22.03 ± 1.36	16.65 ± 0.25	0.82 ± 0.13	1.57 ± 0.39	6.78 ± 0.08	70.3
F2	13.16 ± 0.05	23.00 ± 0.78	17.66 ± 0.24	0.84 ± 0.10	2.25 ± 1.00	6.66 ± 0.10	64.6
F3	12.14 ± 0.92	21.83 ± 0.77	19.49 ± 0.24	1.24 ± 0.41	4.43 ± 1.01	6.72 ± 0.02	62.4
P1	10.49 ± 0.29	22.50 ± 0.78	14.94 ± 0.20	2.51 ± 0.24	6.04 ± 0.33	6.50 ± 0.15	72.9
P2	11.28 ± 0.51	21.28 ± 1.50	13.45 ± 0.23	1.62 ± 0.61	5.14 ± 0.14	6.27 ± 0.05	69.1
P3	11.21 ± 0.59	21.67 ± 0.85	12.52 ± 0.12	1.44 ± 0.27	3.41 ± 0.66	6.26 ± 0.11	65.6
Control	10.24 ± 0.41	26.13 ± 1.18	18.36 ± 0.26	2.05 ± 0.27	5.30 ± 0.87	6.49 ± 0.04	–

Values are given as average ± standard deviation from three replication.

Number followed by the same letter show there is not significantly different ($p > 0.05$)

Table 4 Properties of tablet detergent a disintegration time of effervescent system of 15 s–30 s [1]. However, according to Swarbrick [28] the dissolution time required for effervescent tablets is ≤5 min. The formulation containing zeolite presented the best disintegration time compared to other formulas. Based on the statistical analysis, it was shown that the higher the concentration of zeolite, the worse the desintegration time of tablet detergent becomes because zeolite is not soluble [3]. The disintegration time of effervescent tablets can be hindered by insoluble ingredients, binding materials and an excessive tablet hardness [24].

The pH values (Table 4) of F1, F2, and F3 detergent solutions was found to be in an acceptable limit of SNI requirements (19-7188.2.1-2006). The pH value of < 10.5 measured in a solution according to the washing dose recommended by the manufacturer and SNI (05-4075-1996) is in the range of 6 – 8. Hence, it is safe for the skin. According to Khetrapal and Mudgal [25] detergents with pH 7 (neutral) are more environmentally friendly. Cleansing preparations with acidic pH (< 5) can reduce the cleaning action on stain release [30]. Based on the statistical analysis, it was shown that the difference of the zeolite concentration does not significantly influence the pH value of the detergent solution.

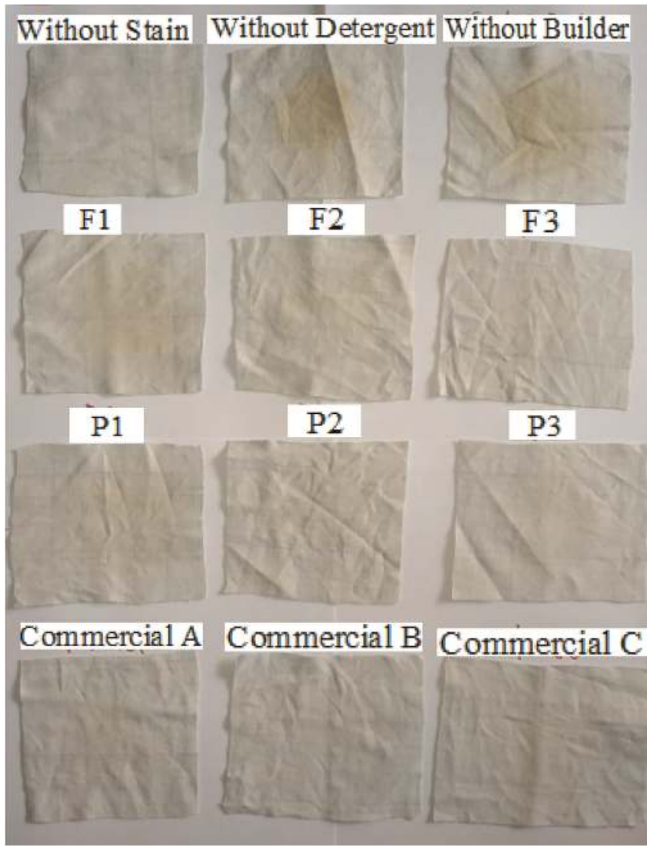
The BOD_5 value of F1, F2, and F3 detergent was 62 %–70 % (Table 4). This result is similar to the report of Khetrapal and Mudgal [25] which asserted that detergent biodegradability must be greater than 60 % on the BOD_5 test. Regarding BOD_5 testing with the Winkler titration method does not show significant differences in biodegradability with the use of phosphate builders and zeolite builders in detergents.

Cleansing actions are related to the detergent's ability to remove stains [25]. Based on these results it can be concluded that the higher the concentration of zeolite, the better the cleaning action of the detergent. Figure 4 presents that all the formulations have a cleaning action performance which closely match to commercial brands. The three reference detergents chosen in this study are the most popular detergents on the market. Generally, those commercial detergents contain: surfactants, builder, enzym and filler. In Indonesia, detergents in the form of tablets are not popular so the powder form was chosen because it is most widely used by the consumers. In addition, the cleansing action test compared the ability of detergent to remove stains to the market to assess the effectiveness of the product [31]. However, further research is needed to assess the effect of tablet detergent with zeolite A as a builder on eutrofication phenomenon.

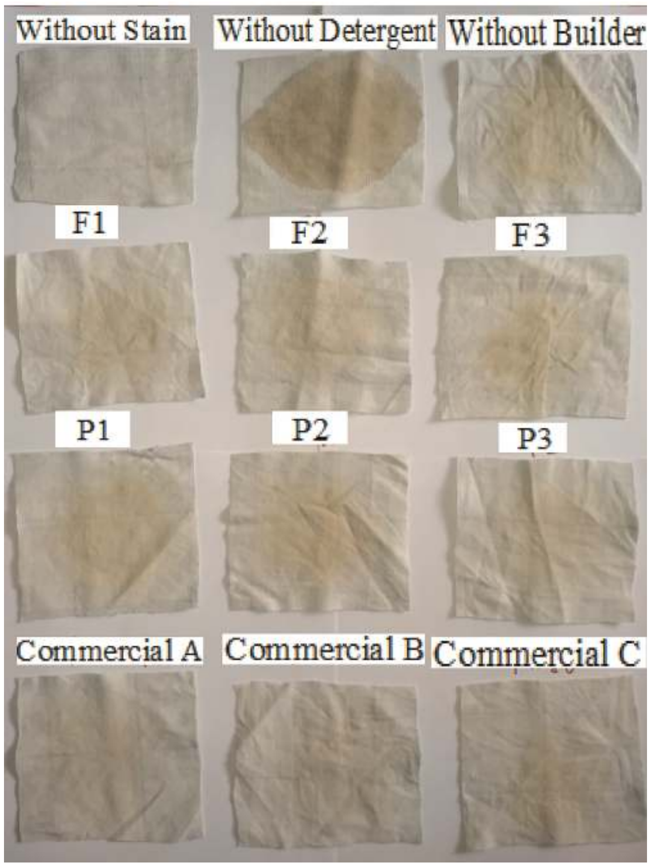
4 Conclusion

The zeolite synthesized from rice husk ash by melting method is a type A zeolite. The FTIR analysis results of synthesized zeolite indicate a T–O bond (T = Si or Al). The XRD pattern showed that the components of zeolite A consist of a crystalline phase mixed with an amorphous phase, with the amorphous phase predominant. The morphology SEM showed cubic particles form of zeolite and the CEC value of 95.71 $cmol^{(+)}$ kg^{-1}.

Formula F1 with 15 % zeolite as the builder is the best formula with granule flow rate parameters 13.6 gram/s, angle of repose of 22.0°, compressibility of 16.6 %, hardness of 0.81 kgf/cm^2, disintegration time of 1.5 min, pH of 6.7 and a biodegradability value of 70.3 % in BOD_5 test. It was shown that the higher the concentration of zeolite, the better the cleaning action of detergent.



(a)



(b)

Figure 4 The cleaning action of detergent for (a) soy sauce stain and (b) tea stains

Acknowledgements

The authors would like to thank the Faculty of Mathematics and Natural Sciences, Tadulako University that financially supported this study via grant scheme of Hibah Penelitian Lektor-2018 with number 5873/UN28.1.28/KP/2018.

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Received: 12. 11. 2019
Revised: 19. 02. 2020

Bibliography

DOI 10.3139/113.110683
Tenside Surf. Det.
57 (2020) 3; page 203 – 210

ISSN 0932-3414

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