Synthesis of Rice Husk-Based Zeolit using Hydrothermal Method and Its Detergent Builder Properties

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Abstract. Detergents are cleaning agents that consist of a complex formulation such as surfactants, builders, bleaching, fillers and other additives. Detergent builder that commonly used is sodium tripolyphosphate (STPP) that are unfriendly environmentally. One of the detergent builders that is more environmentally friendly is zeolite. Therefore, in the present work, zeolite was synthesized using hydrothermal method by varying the temperature and characterised its detergent builder properties. Zeolite was synthesized by mixing sodium silicate (Na_2SiO_3) and sodium aluminate $NaAl(OH)_4$ with the presence of NaOH. Firstly, a mixture of sodium silicate and sodium aluminate formed sol and gradually become gel. After that, the gel had been treated by hydothermal for 7 hours at different temperatures: 50^0C, 100^0C and 150^0C. Several characteristic techniques such as FTIR and XRD were applied to identify functional group and the crystal structure, respectively. Furthermore, the detergent builder properties were characterised using cation exchange capacity (CEC) and detergency test. The result showed that zeolite synthesized at 100 ^{0}C gave better washing capability than others.

Keywords: zeolite, detergent, builder, rice husk, hydrothermal

Introduction

Modern detergents contain complex formulations including surfactant, builder, bleaching agent, filler and other additives [1]. The development of modern detergent provides benefit to humans in term of washing clothes, especially with the presence of builder in its formulation, because the builder will enhance the washing efficiency of surfactant by deactivating or exchanging the cations or minerals causing water hardness which further reduces the effectiveness of detergency [2]. Detergent builder commonly used is sodium tripolyphosphate (STPP) that is environmentally unfriendly since it leads to deposition of phosphate in water which results in eutrophication so that the population of algae or other aquatic plants increase [3]. Therefore, it is necessary to replace this builder with other builders which are more environmentally friendly such as zeolite.

Zeolite can be obtained from nature or by synthesis using sodium silicate and sodium aluminate solution. In order to produce sodium silicate, rice husk ash can be used as source of silica and then the obtained silica is treated using sodium hydroxide. Meanwhile, sodium aluminate is obtained from $Al(OH)_3$ treated using sodium hydroxide. Furthermore, zeolite can be synthesized by several methods such as sol-gel, reflux [4], hydrothermal [5], extraction and melting at high temperatures [6]. However, hydrothermal method gives several advantages such as the crystal growth occurs faster because of the influence of hydrothermal pressure and temperature.

In zeolite synthesis by hydrothermal method, there are several factors that affect crystal growth such as the molar ratio of Si/Al, time of hydrothermal process [7], aging time, base concentration [8] and temperature of hydrothermal process [5].

This paper reports the synthesis of zeolite from rice husk ash as silica source by sol-gel method followed by hydrothermal method under variation of hydrothermal temperature. The obtained zeolite was further applied as detergent builder in the process of detergency. This research finding was expected to produce the synthetic zeolite which has the ability as a good detergent builder to replace sodium tripolyphosphate (STPP).

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Experimental Methods

Materials.

Rice husk ash, sodium hydroxide, aluminium hydroxide, sodium lauryl sulfate, sodium tripolyphosphate, aquadest, aquabidest, sodium sulphate, cotton fabric and mixture of standard dirt consisting of gasoline and fat from beef lard, kaolin, carbon, $FeCl_3$ and acetone. All chemicals are of analytical grade purchased from Merck, Indonesia.

Production of Rice Husk Ash.

Rice husk was washed by aquadest, then dried under the sun. Furthermore, 250 gram rice husk had been roasted using a skillet placed above gas stove for 30 minutes until the black and white rice husks were obtained. The obtained product was then calcined in the furnace (Thermolyne 2116) at 700°C for 4 hours and then cooled back to room temperature (30°C).

Synthesis of Sodium Silicate solution.

5 gram of rice husk ash was dissolved in 100 mL NaOH at the **concentration** of 6.67 M and stirred 1300 rpm accompanied by heating at 80°C for 2 hours. This procedure is in accordance to research undertaken by Prastyo [8].

Synthesis of Sodium Aluminate solution.

20 gram NaOH was dissolved in a little aquadest and then added 8.5 **gram** $Al(OH)_3$ and added more aquadest to get 100 mL total volume. The mixture was subsequently shaken and stirred 2000 rpm accompanied by heating at 100°C until the mixture became solution. The method used followed procedure presented by Prastyo [8].

Sinthesis of Zeolite.

Before doing synthesis, the ratio of Si/Al contained in sodium silicate and sodium aluminate solution was determined by Atomic Absorption Spectroscopy (AAS) (Hitachi Z-8000). 20 mL sodium silicate and 20 ml sodium aluminate were mixed by the sol-gel method and then stirred 1300 rpm for 2 hours until homogeneous solution was obtained. A mixture of sodium silicate and sodium aluminate was inserted into teflon bottle and then the teflon was introduced into the hand-made autoclave stainless steel (hydrothermal autoclave) and then heated in various temperatures, namely, 50°C, 100°C and 150°C for 7 hours in a closed system. The results were then filtered using filter paper Whatmann 42. The solids formed were then washed using aquabidest until the pH of the filtrate reached 10-11. Furthermore, every residue had been dried in oven (scientific oven fisher 630F) at 100°C for 12 hours.

Characterisation of Zeolite.

Characterization of synthetic zeolite was performed using X-Ray Difractometer (XRD) (Shimadzhu X-2000), Fourier Transform Infra Red (FTIR) (Shimadzhu FTIR-8201 PC) to identify the structure of zeolite and the functional groups contained in the zeolite, respectively.

Analysis of Cation Exchange Capacity (CEC).

3 gram of every obtained zeolites synthesized under various hydrothermal temperatures - 50°C, 100°C and 150°C – was analysed using cation exchange capacity analytical quipment in order to determine the total amount of cations contained in zeolites that can be exchanged.

Synthesis of Standard Dirt Solution.

Some of beef lard was mixed in aquadest and stirred 1600 rpm and heated for 2 hours to remove fat from the beef lard. 10 gram fat from beef lard was mixed with 19.32 gram kaolin, 600 mg $FeCl_3$, 80 mg carbon and 5 gram gasoline. The mixture was then suspended in 500 ml acetone. The mixture had been stirred 1600 rpm for 10 minutes until the homogeneous suspension was achieved. This procedure followed the prosedure proposed by Nugroho [9].

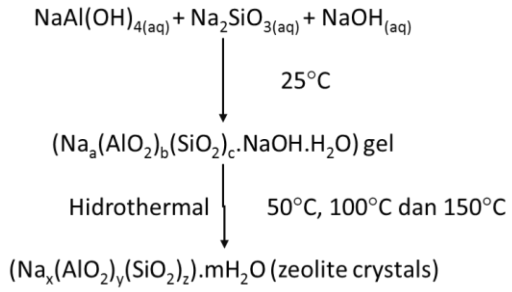
The Detergency Test.

Cotton fabric with a size of 10 x 10 cm had been dried in oven at 105°C for 3 hours till a constant weight of the fabric was achieved. Furthermore, the fabric had been stored in a desiccator for 1 hour. The fabric was then weighed and recorded its mass as Fabric Net Weight (FNW). The clean cotton fabric with the weight constant was introduced in the 1000 mL beaker glass containing solution of standard dirt and stirred for 30 minutes until the dirt was attacted on fabric (substrate). When the dirt was estimated to had been attached to the cloth, the cloth was lifted and aerated for 30 minutes in ambient air. Thereafter, the cloth had been dried again in oven at 105°C for 3 hours and and then stored in a desiccator for 1 hour. The Fabric treated was weighed and recorded its mass as the Fabric Dirty Weight (FDW). The dirty cloth was then washed with detergent solution consisting of 0.23 gram sodium lauryl sulfate (SLS), 0.6 gram zeolite as builder obtained from synthesis under hydrothermal at 50 ^{0}C and 0.17 gram sodium sulfate as filler. The mixture had been stirred for 30 minutes at 1300 rpm. After washing process, the fabric was then rinsed using tap water and aerated for 30 minutes. Hereafter, the cotton fabric had dried in oven at 105°C for 3 hours and stored in a desiccator for 1 hour. The cloth was weighed and recorded its mass as the Fabric Washing Weight (FWW). All these procedure was also applied to other zeolite synthesized at 100°C and 150°C. In addition, the STPP was also used as builder to compare the detergency properties of synthetic zeolits. The detergency test method used is in accordance with the reference reported by Firdaus [10].

Results and Discussion

Synthesis of Zeolite.

The reaction between sodium silicate and sodium aluminate in the presence of sodium hydroxide in the hydrothermal chamber at various temperatures (50 ^{0}C, 100 ^{0}C and 150 ^{0}C) formed metastable amorphous zeolite phase in the form of white colloidal suspension [11]. The Sodium cation (Na^+) from the sodium silicate and sodium aluminate was used to stabilize the units forming the zeolite framework that are Si atom derived from sodium silicate and Al atom derived from sodium aluminate [12]. The reaction mechanism of zeolite formation is below: [13]



$(Na_x(AlO_2)_y(SiO_2)_z).mH_2O$ (zeolite crystals)

Characterization of Synthetic Zeolites

X-Ray Diffraction (XRD). Diffractogram of synthetic zeolite Z-1, Z-2 and Z-3 from rice husk ash is shown in Fig. 1(a), (b) and (c), respectively. The diffractogram of Z-1 zeolite indicated with the highest intensity is at 2 theta (2θ): 29,3033; 26,4383 and 23,3381. The data is in agreement with the database of JCPDS number 39-0222 ($Na_{96}Al_{96}Si_{96}O_{384}.216H_2O$) and JCPDS number 38-0241 ($Na_2Al_2Si_{1.85}O_{7.7}.5.1H_2O$), therefore it is proposed that this zeolite is Na A zeolite with a cube-shaped crystal structure. The second synthetic zeolite (Z-2) demonstrated the highest intensity peaks at 2 theta (2θ): 29,2187; 26,3687 and 23,2618. These data are in agreement with the database of JCPDS number 39-0222 ($Na_{96}Al_{96}Si_{96}O_{384}.216H_2O$) and JCPDS number 38-0241 ($Na_2Al_2Si_{1.85}O_{7.7}.5.1H_2O$). Based on these JCPDS number, the type of this zeolite is also Na A zeolite with a cube-shaped crystal structure. In the meantime, the synthetic zeolite of Z-3 showed the highest intensity peaks at 2 theta (2θ): 13,4527; 23,7785; 30,9885 and 34,1597. Based on the database of JCPDS number 43-0168 ($Na_2Al_2Si_{4.5}O_{13}.xH_2O$), this zeolite has diffractogram pattern similar with Na Y zeolite with cube-shaped crystalline structure. Synthesis of zeolite carried out under hydrothermal temperature at 150°C gave different pattern on its diffractogram compared to zeolite synthesized under hydrothermal temperatures at 50°C and 100°C. This could occured due to the rearrangement of bonds between Si-Al during the hydrothermal process at 150°C which further resulted in the change of the zeolite framework structure.

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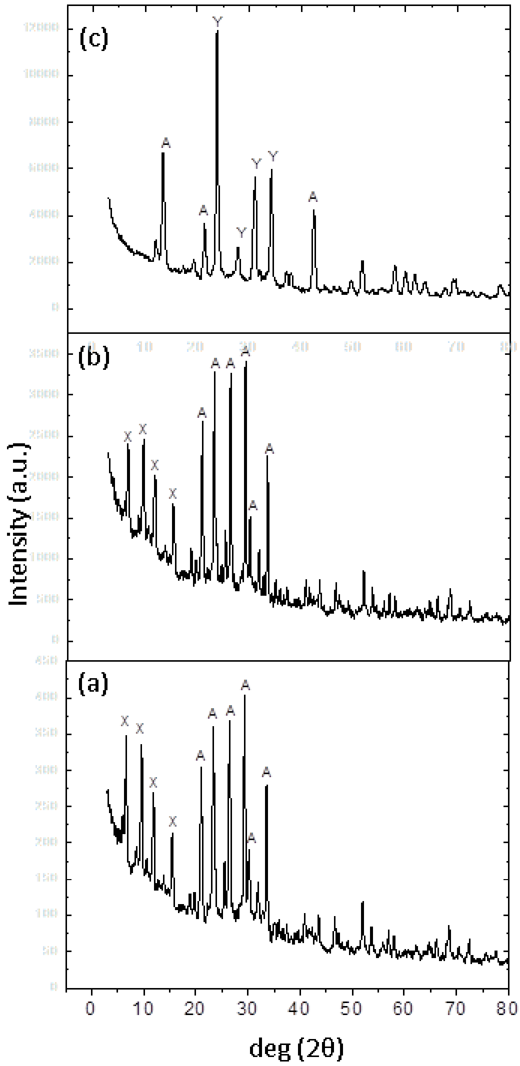

Figure 1 Diffractogram Synthetic Zeolite under Hidrothermal Temperature (a) 50°C (Z-1) (b) 100°C (Z-2) and (c) 150°C (Z-3)

Fourier Transform InfraRed (FTIR). Figure 2(a), (b) and (c) shows respectively the FTIR spectra of zeolites Z-1, Z-2 and Z-3 synthesised in diffferent temperatures during hydrothermal process. FTIR spectra of three samples are almost the same. The vibration modes at 1018,41 cm^{-1}, 1010,70 cm^{-1} and 1010,70 cm^{-1} are atributed to the asymmetric stretching vibration of OSiO / OAlO. Moreover, the bands at 663,51 cm^{-1} and 462,92 cm^{-1} observed in all samples correspond to the symmetry stretching vibration of OSiO / OAlO and bending vibrations of OSiO / AlO. The vibration mode observed at 555.50 cm^{-1} in samples Z-1 and Z-2 is attributed to the vibration of the double ring. This vibration mode is detected at 570.93 cm^{-1} for sample Z-3. All these observed vibration modes were identified in NaA and NaY zeolites [14, 15].

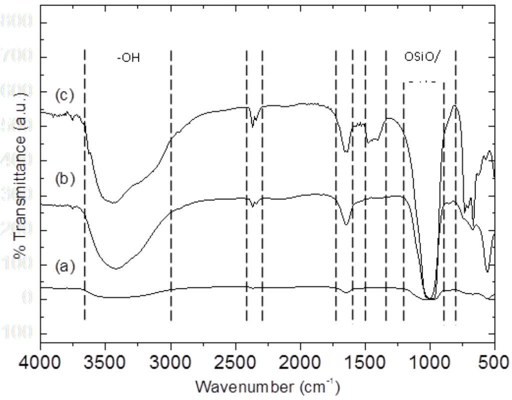

Figure 2 FTIR spectra of Synthetic Zeolite under Hidrothermal Temperature 50°C (Z-1) (b) 100° C (Z-2) and (c) 150°C (Z-3)

Cation Exchange Capacity. Cation exchange capacity (CEC) was applied to determine the amount of cations presence in zeolites that can be exchanged by cations from other materials in a system such as hard water. The CEC of synthetic zeolites is presented in Fig. 3. The CEC values of synthetic zeolites Z-1, Z-2 and Z-3 were 50.80 meq/100 gram, 80.80 meq/100 gram and 132.80 meq/100 gram, respectively. These results are lower than that of reported by Cardoso et al (2015) in which the CEC of 4A zeolite synthesized from fly ash was 450 meq/100 gram. Moreover, Qian and Li [5] reported that the CEC of the Na A zeolite synthesized from coal gangue (fly ash) was 358 mg/gram. The low value of the cation exchange capacity (CEC) synthetic zeolites maybe caused by the presence of Si and Al atoms as the zeolite components were bound unorder so that the zeolite formed consisted of imperfect Si-Al bond so that the amount of sodium ions having role as cations neutralizing negatively charged Al atom were lower than that of 4A zeolite. The most important finding is that the highest CEC was achieved in Z-2 synthesised at 100 ^{0}C during hydrothermal process.

The Detergency Test. Detergency is the process of removing undesirable substances (dirt) from a solid surface (substrate) with various physicochemical and mechanical ways related to the performance of surfactants in detergents. Detergency is colloid phenomenon that reflects the physicochemical behavior of matter at the interface related to the removal of dirt and oily mixtures from solid substrates. Detergency process occurs by adsorption of surface active agents (surfactants) to the solid surfaces of the detergent solution so that undesirable substances can be removed from the system [16].

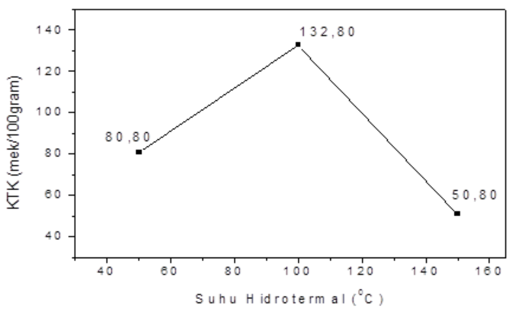

Figure 3 CEC of Synthetic Zeolite

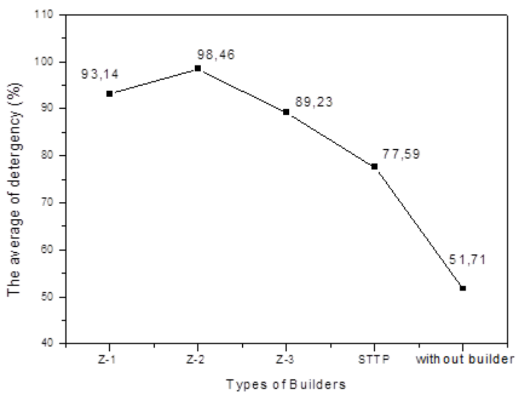

Figure 4 Comparison of detergency Test on Zeolite Synthetic with Builder STPP

In the detergency test, the role of builder is to improve the washing efficiency of the surfactant by deactivating minerals containing calcium and magnesium ions that lead to hard water. Calcium and magnesium ions were exchanged by sodium ions containing in zeolite. This cation exchange enhanced the performance of surfactants in detergency process because the surfactant increases the contact angle between the substrate and the dirt so that the dirt was more easily removed from the substrate.

Figure 4 presents the results of detergency test of three samples Z-1, Z-2 and Z-3 used as builder in detergent. It can be seen that these samples showed higher washing efficiency than STPP which is commonly used in commercial detergent. The percentage of the detergency are 93%, 98% and 89% for Z-1, Z-2 and Z-3, respectively. The highest detergency was given by Z-2 synthesised under hydrothermal method at 100 ^{0}C. This result is in agreement with CEC value as demonstrated in Fig. 3. Moreover, this result is also in agreement with Qian and Li [5] report which showed the correlation between the CEC value and the increase of the hydrothermal termperature. The CEC value increased when the hydrothermal temperature was set up to 90 ^{0}C. On the other hand, it decreased when the temperature was set up higher than 90 ^{0}C.

Conclusion

1.The synthetic zeolites synthesized under hydrothermal process at temperatures 50°C (Z-1) and 100°C (Z-2) predominantly produced Na A zeolites with value of cation exchange capacities (CEC) 80,80 meq/100 gram and 132.80 meq/100 gram, respectively. In the meantime, the synthetic zeolite fabricated under hydrothermal at 150°C (Z-3) predominantly resulted in Na Y zeolite with a value of cation exchange capacity (CEC) 50,80 meq/100 gram.

2. The detergency test of zeolite synthesized under hydrothermal at 50 ^{0}C and 100 ^{0}C showed an increase on the rate detergency percentage; however, it decreased when Z-3was applied. The optimum percentage of rate detergency was achieved up to 98% for zeolit Z-2.

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