Preparation and characterization adsorbent based on zeolite from Klaten, Central Java, Indonesia

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Abstract. The aim of this study was to prepare and characterize a potential adsorbent based on zeolite from Klaten, Central Java, Indonesia. The pre-treatment of natural zeolite (ZA) consists of chemical activation using HCl (ZAA) and NaCl (ZAT). Cationic surfactant benzalkonium chloride was used for modification of the zeolitic surface. ZA, ZAA, ZAT, and modified zeolites were characterized by FTIR, XRD, and AAS. The cation exchange capacity (CEC) of the natural zeolite measured by 1 M NH4OAc method. Results show that the higher Si/Al ratio was achieved when natural zeolite was activated by the strong acid of HCl, but acid activation did not change the structure of the zeolite itself. The result of XRD analysis supports the AAS analysis result in which the degrees of crystallinity of zeolite increased after acid activation. The studies by FTIR and XRD analysis indicated that the zeolite structure remained unchanged after the modification with the cationic surfactant. Thus the activated and modified zeolites create a new material adsorbent to reduce pollutants in the environment.

1. Introduction

Indonesia has a large number of minerals including natural zeolite. Zeolites are crystalline hydrated aluminosilicate material with three-dimensional frameworks that based on TO4 tetrahedra, where T is an aluminium or silicon atom (phosphorus in aluminophosphates) arranged regularly in which each oxygen atom is divided between two tetrahedra [1]. Zeolites have a great potential as effective sorbents for water treatment applications, such as dyes, heavy metals, and other pollutants from wastewater and natural waters. Zeolite modification extends obviously the zeolites application. The surface properties of zeolites may be greatly modified with cationic surfactant by ion-exchange reactions [2].

To improve ion-exchange capacities, it is important to modify their chemical structure and composition by applying a suitable pretreatment. In this paper, the natural zeolite (ZA) was activated with different activating agents. The objectives of this study are determining the Si/Al ratio of the zeolite after HCl or NaCl pretreatment. HCl is frequent reagent used to activate the natural zeolite. The ability of HCl-activated natural zeolite was higher than the natural zeolite without activation that is used to remove of rhodamine B from aqueous solution [3]. Ion exchange with sodium chloride solution is widely employed because sodium ions can readily remove other cations and therefore enhancing the adsorption capacity.
This research was aimed to characterize the zeolites by using of NaCl and HCl to activate the natural zeolite. A negatively charged framework and its hydrophilic properties cause the zeolite to be inappropriate for the binding of anionic and hydrophobic species [4]. However, adsorption of surfactants can modify the properties of the zeolite surface [5]. Therefore, this adsorbent has a good affinity toward inorganic pollutants, but little or no ability to remove organic pollutants. The surface properties of zeolites may be greatly modified with cationic surfactant by ion-exchange reactions. Currently, many research studies have investigated the modified zeolite using cetyl trimethyl ammonium bromide (CTAB), hexadecyl ammonium bromide (HDTMA), and sodium dodecyl sulfate (SDS) [6-7]. By the addition of cationic surfactants, the zeolite surface can be modified to improve the anion exchange capacity and, to an extent, the potential to eliminate cations, anions, and organic compounds [8-10].

For this purpose, modification of the zeolite surface was performed using cationic surfactant benzalkonium chloride, in which each molecule is composed of a hydrophilic and positively charged head group and a hydrophobic tail. Benzalkonium chloride may form monolayers and/or bi-layers on the zeolite surface [11].

2. Experimental Section

2.1. Materials and reagents
Natural zeolite (ZA) from Klaten Central Java Indonesia was used as starting material. Reagents of analytical purity NaCl, HCl, benzalkonium chloride were used on the activation and modification, respectively. Benzalkonium chloride supplied by Sigma. Aquabides was used to the solvent for making the chemicals solution. The chemical structure of quaternary ammonium salt benzalkonium chloride is shown in figure 1 was used as a cationic surfactant.

![Figure 1. Chemical structure of benzalkonium chloride](image)

2.2. Preparation and activation of the natural zeolite
ZA was crushed and sieved to yield particle 250 mesh. Some 50 g of ZA was weighed, then washed and dried in an oven at 80 °C for 24 hours. Washing and drying step were carried out prior to characterization of ZA chemical properties. Atomic Absorption Spectroscopy (AAS) was utilized for revealing the composition of the cation oxide chemical compound in the ZA [12]. The result of AAS analysis was used to calculate the Si/Al ratio inside the ZA. X-Ray Diffraction (XRD) powder diffraction was used to confirm the composition analysis result. Characterization of functional groups of ZA was used Fourier Transform Infrared Spectroscopy (FTIR). Activation of the zeolite was carried out by contact of the powdered material with an aqueous solution of NaCl and HCl. Solutions of HCl 3 M and NaCl 0.1 M were prepared as an activating agent.

A known quantity of ZA (1 g) was mixed with 100 mL of NaCl solution 1 M for 24 hours, at room temperature. Then, the suspension was filtered and the material washed with aquabides. The wet activated material was dried at 105 °C for 24 hours and used in the modification step. The product of this process is called the activated zeolite (ZAT).

Afterward, The ZA was submerged in 150 mL HCl solution 3 M and dried for 30 minutes at 72 °C. The mixture was filtered and washed with aquabides until neutral (pH=7), dried in an oven at 110-120 °C for 3 hours. Then, the product was diluted with 100 mL of NaCl solution 1 M and stirred for 24
hours at room temperature. The suspension was filtered with aquabides and dried at 105°C. The product of this process is called activated zeolite (ZAA).

Studies of cationic exchange capacity (CEC) of the ZA, ZAT, and ZAA used the reagent of analytical purity NH₄OAc. The mineralogical compositions of the zeolite were determined by X-ray diffraction analyses (XRD) with an automated Rigaku multiflex diffractometer with Cu anode using Co Kα radiation at 32 kV and 20 mA over the range (2θ) of 2-65° with a scan time of 4 °/min. The crystalline phases present in the zeolitic materials were identified with the help of ICDD (International Centre for Diffraction Data).

2.3. Modification of the activated zeolite
The modification of the ZAT and ZAA was performed contacting the powdered material samples with benzalkonium chloride (BC). Thus, 1 g of the ZAT was contacted with 100 mL of the BC solution equivalents of twice as of its CEC for 24 hours at room temperature. The suspension was filtered, washed with aquabidest, and dried at 60°C for 24 hours [11]. The similar process was repeated by substitution of ZAT with ZAA. The obtained products denoted as ZATB and ZAAB. Both ZATB and ZAAB will be examined by XRD and FTIR analysis.

FTIR spectra of the natural zeolite, activated zeolite, and modified zeolite was recorded in the range of 400-4000 cm⁻¹ using a Shimadzu FTIR-8201 PC. The zeolitic materials were dispersed in KBr and compressed into disks.

3. Results and Discussion

3.1 Characterization by Atomic Absorption Spectroscopy (AAS)
The chemical composition of the ZA, ZAT, and ZAA determined by AAS is shown in table 1. Natural zeolite (ZA), besides contain the negative charge compensator such as alkali and alkaline earth cations, it also contains the undesired component such as oxides of metals. The metal oxides are trapped in the frame of zeolite when it is formed naturally. The existence of those oxide contaminants could decrease pore sizes and thereby decrease the ability of zeolite matrices as an adsorbent. By activation, those contaminants would be discarded the zeolite matrices.

| Components | ZA (%) | ZAT (%) | ZAA (%) |
|------------|--------|---------|---------|
| Si         | 27.96  | 26.30   | 28.34   |
| Al         | 9.20   | 9.00    | 8.52    |
| K          | 0.75   | 0.50    | 0.55    |
| Na         | 1.19   | 1.70    | 1.80    |
| Ca         | 0.83   | 0.70    | 0.60    |
| Si/Al ratio| 3.04   | 2.92    | 3.33    |

The characterization results of the samples with different activating agent and concentration show a significant change after the activation. The AAS analysis results have been used to calculate the Si/Al ratio as reported in table 1.

The Si/Al ratio of the ZAA increase was also followed by the increase of adsorptivity because the releasing of Al from the active site Si-O-Al caused the transformation of the active site into Si-O-Si in which the Si was coming from the outer structure. But, keep in mind that the zeolite tends to be a hydrophobic adsorbent when the Si/Al ratio increased. The formation of the localized electrostatic pole between cation and anion resulted in hydrophilic characteristic to adsorb polar pollutant well. The releasing of aluminium (dealumination) would reduce the number of cation inside the zeolite structure and reduced the hydrophilic characteristic of the zeolite. The removal of the Al atom from ZA framework increases the Si/Al ratio of ZAA. Characterization of ZA, ZAT, and ZAA using AAS (Table 1) shows that the Si/Al ratio after the acid activation increase from 3.04 to 3.33 for ZA and
The Si/Al ratio for zeolites is associated with the cation exchange capacity. ZA showed low values of Si/Al ratio (92.80 me/100 g) indicating materials with high cation exchange capacity [13]. The CEC values of the ZAT (99.09 me/100 g) were higher than ZAA (54.40 me/100 g). This result indicated that negative charge of zeolite decrease thus capability to exchange the cation decrease too.

3.2. Characterization by Fourier Transform Infrared Spectroscopy
The natural zeolite and activated zeolite were characterized by FTIR spectroscopy, and their IR spectra are shown in figure 2. The features positioned at 3441.0 cm\(^{-1}\) is characteristic bands of the mordenite connected to the vibration of the hydrogen-bonding hydroxyl groups. A band at 1635.64 cm\(^{-1}\) is associated with the deformation vibration of the absorbed water, whereas the band at 1049.28 cm\(^{-1}\) is related to the asymmetric valence vibration in the SiO\(_4\) tetrahedra [11]. No variations in the frequency of these bands in the spectra of ZA, ZAT, and ZAA samples were observed, confirming that differential activation of zeolite does not affect the zeolite structure.

![Figure 2. FTIR spectra of ZAT (a), ZA (b), ZAA (c)](image)

However, three new bands appear, implying the presence of BC on the composite, two bands assigned to the C-H stretching vibrations of the hydrocarbon chain, 2924.09 and 2854.65 cm\(^{-1}\), and a third one band corresponding to the C-H bending of the methyl and methylene groups at 1465.9 cm\(^{-1}\). The IR spectra for modified zeolites are shown in figure 3.

![Figure 3. FTIR spectra of BC (a), ZATB (b), ZAAB (c)](image)
No relevant variations in the frequency of the band assigned to the ZAA and ZAT after the treatment with the BC were observed, which indicates that the zeolite structure remains unaltered after the modification.

3.3. Characterization by X-ray Diffraction (XRD) analysis

Diffracrogram of natural zeolite results in table 2 shows the intensity at an angle $2\theta = 25.66$ Å, 22.24 Å and 26.68 Å. There is a maximum peak at an angle of $2\theta = 25.66$ with a distance of 3.47Å. These results provide diffraction pattern shown in the display figure 4(c).

Table 2. Results of X-ray Diffraction analysis of natural zeolite

| $2\theta$ | d(Å) | I/I1 | Intensity (Counts) |
|----------|------|------|--------------------|
| 9.66     | 9.15 | 65.6 | 223                |
| 22.24    | 3.99 | 74.4 | 253                |
| 25.66    | 3.47 | 100  | 340                |
| 26.68    | 3.34 | 71.2 | 242                |
| 27.74    | 3.21 | 52.6 | 179                |

X-ray diffractograms of natural zeolite, activated zeolites, and modified zeolites are shown in figure 4.

Figure 4. XRD graph of zeolite; (a) ZAA, (b) ZAT, (c) ZA

Figure 4 showed that the natural zeolite and activated zeolite composed of crystalline structures. The powder contains a mixture of zeolite mineral groups and the inert minerals. Mordenite was one of zeolite forming minerals found in the zeolitic stone spread in Central Java Indonesia. From diffractogram resulted from XRD analysis, this mineral had the peak value of d 13.89 Å, 9.15 Å, 6.61 Å, 3.47 Å, 3.38 Å and 3.21 Å. Mordenite had such physical property as the orthorhombic structure with 28% void volume. Other zeolite forming minerals existed in diffractogram were albite (NaAlSi$_3$O$_8$), muscovite (KAl$_2$Si$_3$AlO$_10$(OH)$_2$), pyrite (FeS$_2$), chlorite (Mg,Al)$_6$(Si,Al)$_4$O$_10$(OH)$_8$, and quartz (SiO$_2$). Based on the XRD analysis, mordenite zeolite type was the major component in the zeolite. Mordenite zeolite type is a common zeolite found in silica-rich rocks [14].

The pretreatment by HCl and NaCl sharpened the peak in the spectra as shown in figure 4. Thus, this process can increase the crystallinity of zeolite. Application of HCl and NaCl for zeolite activation cause the angle of the peak to become sharper (the angle got smaller). The figure 4 shows that there was no significant change in the XRD patterns before and after activation.
4. Conclusions
Natural zeolites from Klaten Central Java Indonesia have, in its crystalline structure of mordenite. Activated and modified zeolite mordenite with BC is prepared without altering the starting zeolite structure. The adsorption potential of the Klaten natural zeolites can be studied by HCl and NaCl activation. The acid activation of ZA could increase the Si/Al ratio and decrease the CEC which correspond to the low hydrophilic characteristic of the zeolites.

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