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Identification and Enrichment of Indonesian Zeolite using Cation Flotation Method

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Abstract
The cation flotation method was employed to enrich the A-modernite fraction by observing the change of the mixture density, pH, type and concentration of collector and concentration of HF as a function of the floated quantity of this A-morderite.
X-ray diffraction analysis using Shimadzu XD-D1 was conducted to examine the specimens for several variations and settings. The d-spacing identifications were done by comparing the experimental data with the ICDD database and then quantitative analyses were performed. Before the treatment, the existence of A-mordenite in this natural product was confirmed, it has space group Fd3m with lattice parameters a = (24.46 ± 0.96) Å. The average weight concentration before the treatment was 41,02%. The remaining mineral was identified as epistilbite $Ca_3Si_9Al_3O_{24}.8H_2O$, clinoptilolite $[KNa_2K_2]$ $Al_2Si_{10}O_{24}7H_2O$ and B-mordernite $[CaNa_2K_2]Al_2Si_{10}O_{24}.7H_2O$.
After the treatment, higher concentration of A-mordenite was obtained by setting a higher collector concentration, lower HF activator, and pH value to the value 5.0. The highest concentration of A-mordenite was achieved when the setting was 66.45%. The crystallographic structure remained the same since there were neither violent chemical reactions nor heating in all the processes.

Keywords: *Zeolite, X-ray Method, Mordenite, Floatation*

Abstrak
Hampir seluruh zeolit di Indonesia berisi mordenit tipe A, $[Na_2CaK_2]$ $Al_2Si_{10}O_{24}.7H_2O$. Material ini memiliki banyak manfaat di bidang lingkungan, pertanian dan energi; dimanfaatkan untuk penyerap dan penukar ion, namun demikian kemurnian bahan alam ini sangat rendah untuk langsung digunakan. Dalam penelitian ini telah digunakan metoda flotasi untuk memperkaya modernit-A dengan mengamati perubahan beberapa faktor seperti kerapatan campuran, pH, tipe dan konsentrasi kolektor serta HF sebagai fungsi pengambangan material ini.
Analisis difraksi sinar-x dengan menggunakan Shimadzu XD-D1 telah dilakukan untuk menguji sampel para berbagai perlakuan ini. Identifikasi jarak antar bidang dilakukan dengan membandingkan data eksperimen dan database ICDD, kemudian analisis kuantitatif dilakukan. Sebelum perlakuan, keberadaan modernit tipe A dalam bahan alam ini dapat dikonfirmasi, material ini memiliki space group Fd3m dengan parameter kisi a = (24.46 ± 0.96) Å. Konsentrasi berat rata-rata sebelum perlakuan adalah 41,02%. Mineral ikutan yang lain dapat diidentifikasi sebagai epistilbite $Ca_3Si_9Al_3O_{24}.8H_2O$, clinoptilolite $[KNa_2K_2]$ $Al_2Si_{10}O_{24}7H_2O$ dan B-mordernite $[CaNa_2K_2]Al_2Si_{10}O_{24}.7H_2O$.
Setelah perlakuan, konsentrasi modernit-A tercapai dengan membuat konsentrasi kolektor lebih tinggi, aktivator HF yang rendah dan nilai pH sekitar 5.0. Konsentrasi modernit-A tertinggi mencapai 66.45%. Struktur kristalografi tetap sama karena dalam proses tidak ada reaksi kimia atau pun pemanasan.

Kata Kunci: *Zeolit, Metoda sinar-X, Mordenit, Pengambangan*

1. Introduction

Indonesia is a country that has rich natural resources to utilize; zeolite is one of potentially useful natural products of great commercial value. This material is a silicate mineral found in volcanic and sedimentary rocks in arid regions and on the seafloor. It also occurs as crystals in pockets within basalt flows and other volcanic deposits. Zeolites have unusual properties that make them valuable as filtering agents, and a number of synthetic zeolites have been developed to take advantage of these properties[1)]. Most of natural zeolite in Indonesia contains mordenite type A, $[Na_2CaK_2]$ $Al_2Si_{10}O_{24}.7H_2O$[2)]. This type has many valuable applications in agriculture, environment and energy, however the purity of this natural product is too low for direct use.

The purpose of this research was to find a good purification method. The cation flotation method was used to enrich the A-modernite fraction by varying the control parameters like mixture density, pH, type and concentration of collector and concentration of HF. We used x-ray diffraction spectrum to identify the material, to

investigate the crystallographic parameters and to calculate the floated quantity of this A-morderite. The optimum condition is discussed.

2. The Zeolite Structure and Floatation Method

The structure of zeolite atoms causes unusual properties. Zeolites are framework of aluminum silicates, are composed of tetrahedral atomic groups of SiO(4) and AlO(4), and are linked to form three-dimensional complex networks. Other ions, chiefly sodium (Na) and calcium (Ca), are housed in cavities in the frameworks. The zeolites are like the feldspar and feldspathoid minerals, two other groups of framework silicates[3].

Flotation method is a process of automatic carrying/floating solid or fluid above the surface following air movement. The material must be in a hydrophobe condition in order to be attached to the bubble air. This state could be achieved by adding several reactants (flotation reactant) like collector, frother, depressant, and moisture. The choice of the material depends on the mineral used. This technique is often applied for particle separation[4].

3. Sample Preparation and X-ray Diffraction Experiment

We obtained the zeolite natural product ('kasongan') from Dinas Pengendalian Mutu Pertamina (Quality Control Division of the National Mine and Petroleum Company) Jakarta. To carry out the flotation technique, we used the following chemicals: dodesylamin, hexadesylamin, octadesylamin, HF, alcohol 96%, NH_4Cl and distillated water. Those chemicals were used since they have a very good effect in creating the necessary hydrophobe condition. More detailed description can be found elsewhere[4].

Combination of the chemicals, the pH scale and the density of the mixture were varied to find the optimum condition i.e. until we obtained the highest mass percentage of the zeolite. The following combination was prepared:

- zeolite and dosesylamin flotation at pH 5.0, 6.0, 7.0 and 8.0
- zeolite and dodesylamin flotation at pH 6.0, 7.0 and 8.0
- zeolite and octadesylamin flotation at pH 6.0, 7.0 and 8.0

The collector type and the concentration of the collector to the mordenite within floated zeolite were observed as well. The floated specimen was then dried up and was examined by x-ray diffraction.

The x-ray diffraction experiment was conducted using Shimadzu XD-1. We have utilized the standard diffractometer method, and taken wide angle 2θ from 5^o to 90^o. In particular specimen, the experiment was done only up to $2\theta = 50^o$ since there were no diffraction peaks any more after the angle. The Figures 1 to 8 show the XRD spectrum for several conditions.

The spectrum was analyzed by means of the Bragg's law:

$$2\, d \sin\theta = \lambda$$

where d is the interplanar distance, θ is the diffraction angle and λ is the x-ray wavelength. We employed the standard search match method to obtain the crystallographic parameters and we compared with the ICDD (International Centre for Diffraction Data) results[5].

As the control specimen, a pure synthetical mordenite was employed. Its XRD spectrum for comparation was taken using 2θ from 5^o to 90^o (Figure 1). The *d*-spacings were then calculated, and the FWHM (full width half maximum) at the highest diffraction peaks was noted. The area under the peak will be used for quantitative analysis.

4. Results and Discussion

Before the treatment, the existence of A-mordenite in this natural product was tested that, it has space group $Fd3m$ with lattice parameters a = (24.46 ± 0.96) Å. The average weight concentration before the treatment was 41,02%. The remaining mineral was identified as epistilbite $Ca_3Si_9Al_3O_{24}.8H_2O$, clinoptilolite $[KNa_2K_2]$ $Al_2Si_{10}O_{24}7H_2O$ and B-mordernite $[CaNa_2K_2]Al_2Si_{10}O_{24}.7H_2O$.

The weight of the concentration is calculated using the approximation:

$$C_x = \frac{I_x}{I_{std}} \frac{\rho_x}{\rho_{std}} \frac{\mu_{ta}}{\mu_{tb}} C_{\text{std}}$$

where C_x is the estimated weight concentration, I_x and I_{std} are the area below the peak's intensity for the specimen and the standard; ρ is the mass density; μ is the linear absorption coefficient and C_{std} is the standard weight concentration. The XRD spectra of pure zeolite and pure synthetical mordenite are used simultaneously as the standard concentration.

Figures 1 to 8 show the x-ray diffraction spectra for several zeolite settings.

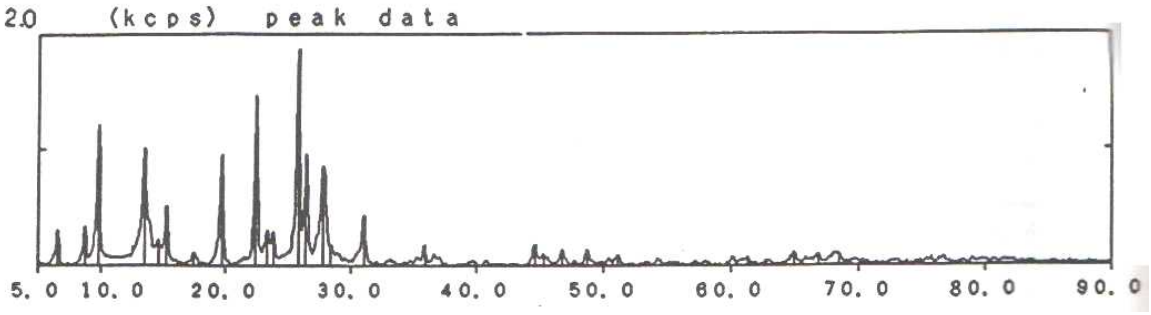

Figure 1. XRD spectrum for pure synthetical mordenite

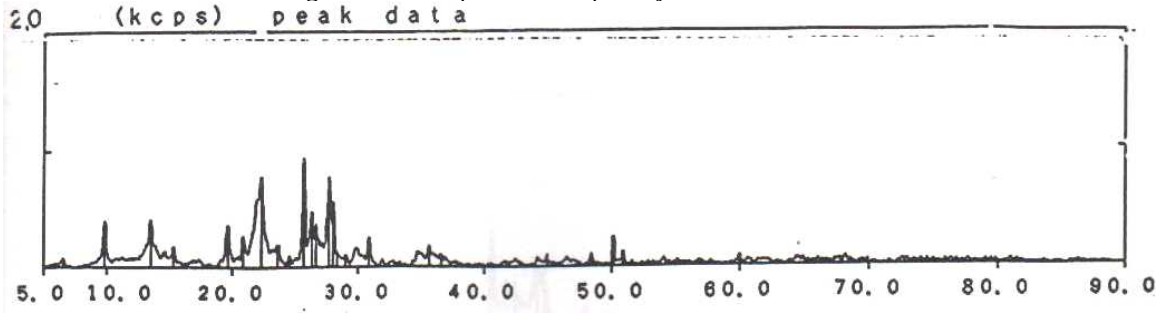

Figure 2. XRD spectrum for pure zeolite

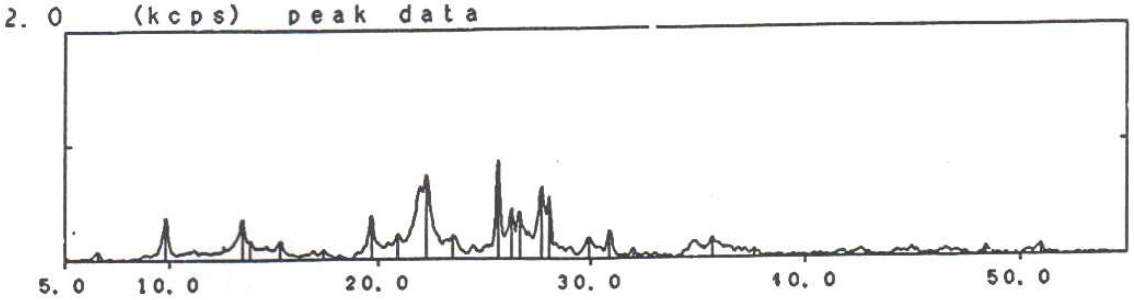

Figure 3. XRD spectrum for zeolite by dosesylamin flotation at pH 6.0

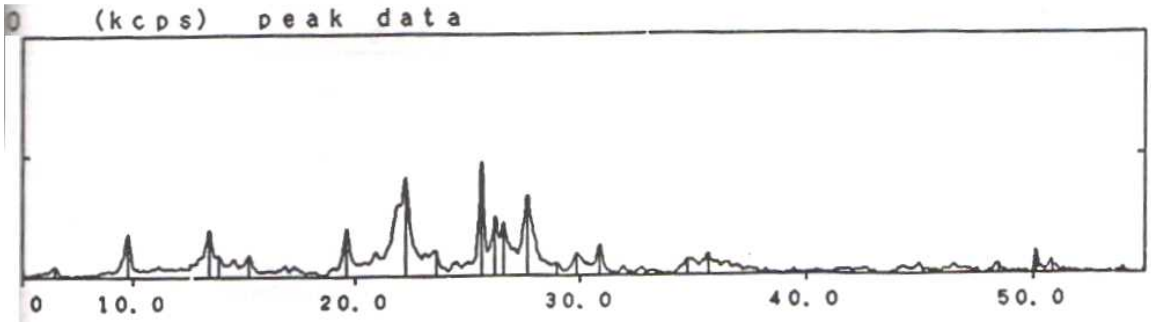

Figure 4. XRD spectrum for zeolite by dodesylamin flotation at pH 5.0

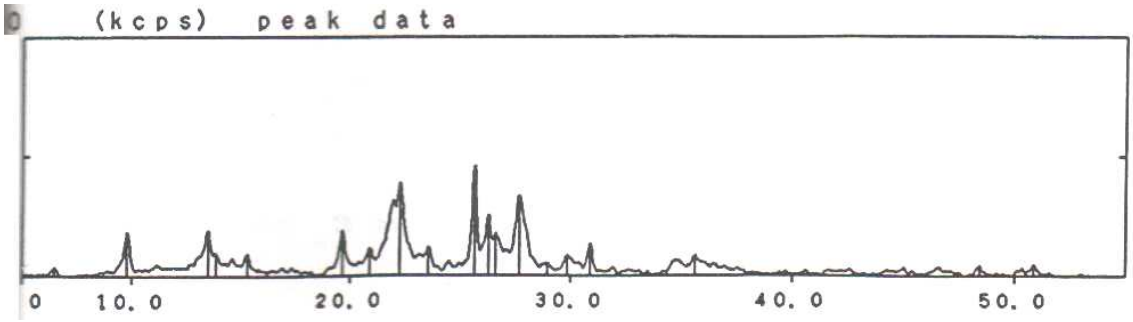

Figure 5. XRD spectrum for zeolite by hexadesylamin flotation at pH 6.0

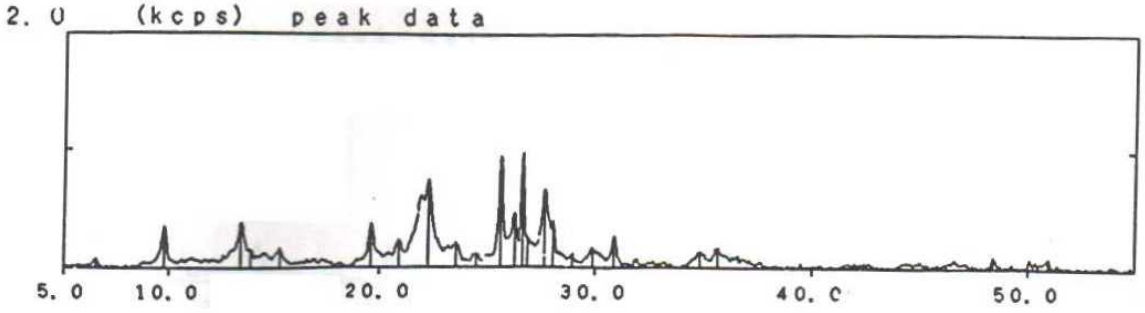

Figure 6. XRD spectrum for zeolite by hexadesylamin flotation at pH 7.0

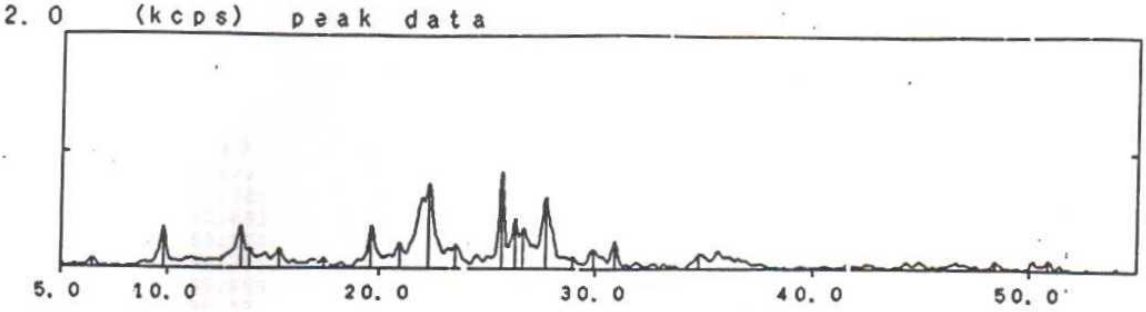

Figure 7. XRD spectrum for zeolite by hexadesylamin flotation at pH 8.0

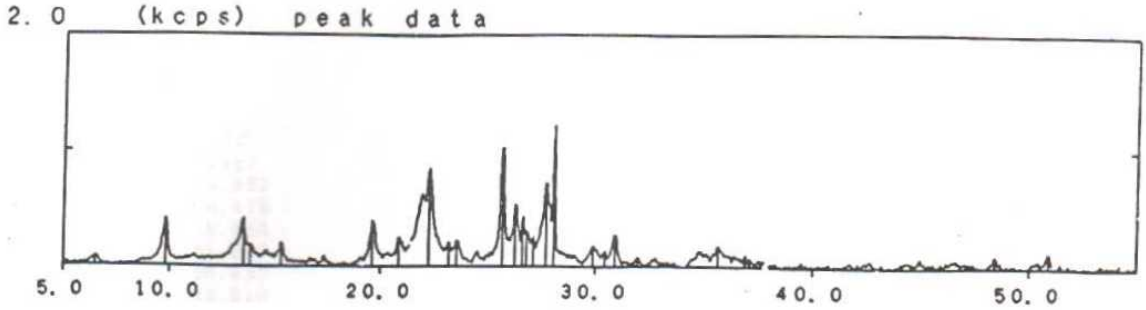

Figure 8. XRD spectrum for zeolite by octadesylamin flotation at pH 6.0

The figures show that except for the pure synthetical mordenite, the other diffraction spectra indicate basically the same features. Only slight change in the 2θ peaks, however the are below the curve varies according to the sample preparation. This shows that after the treatment, the crystallographic structure remained the same; the mordenite sample still has space group *Fd3m* with relatively unchanged lattice parameter. We found the optimum condition is reached on setting pH around 5.0, high collector concentration and lower HF activator. The best concentration of A-mordenite achieved was 66.45%. The improvement of the quality was also reflected in the XRD spectrum.

5. Conclusion

We can conclude that before the treatment the existence of A-mordenite in zeolite natural product was tested that, it has space group *Fd*3*m* with lattice parameters a = (24.46 ± 0.96) Å. The result is similar to the one from ICDD. Its average weight concentration was 41,02%. The remaining mineral was identified as epistilbite $Ca_3Si_9Al_3O_{24}.8H_2O$, clinoptilolite $[KNa_2K_2]Al_2Si_{10}O_{24}7H_2O$ and B-mordernite $[CaNa_2K_2]Al_2Si_{10}O_{24}.7H_2O$. After the treatment, higher concentration of A-mordenite was obtained by setting higher collector concentration, lower HF activator and pH value to 5.0. The highest concentration of A-mordenite achieved by the setting was 66.45%. The crystallographic structure remained the same since there was neither violent chemical reactions nor heating in all the processes.

References

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