Indonesian Physical Review
Volume 6 Issue 1, January 2023
P-ISSN: 2615-1278, E-ISSN: 2614-7904

Morphologycal, Elemental Content, and Physical Properties of Cleaned Clinoptitolite Zeolite (10X) Using Sonication and Microwave

Endah Puspita[1*], Marzuki Naibaho[2], Ramlan[1], Masno Ginting[2*]
[1] *Physics department, Faculty Mathematics and Natural Science University of Sriwijaya, Indonesia*
[2] *Center for Advanced Materials Research (PRMM), National Research and Innovation Agency (BRIN), Indonesia*

Corresponding Authors E-mail: endahpuspita1908@gmail.com, masno.ginting@gmail.com

Article Info

Article info:
Received: 04-12-2022
Revised: 13-01-2023
Accepted: 14-01-2023

Keywords:
Zeolite clinoptitolite, microwave, alumina-silica

How To Cite:
P. Endah, M. Naibaho, Ramlan, and M. Ginting,"Morphologycal, Elemental Content, and Physical Properties of Cleaned Clinoptitolite Zeolite (10X) Using Sonication and Microwave",Indonesian Physical Review, vol.6, no. 1, p 95-104, 2023

DOI:
https://doi.org/10.29303/ipr.v6i1.204.

Abstract

This research was conducted to determine the morphology, elemental content and physical properties of the zeolite samples before and after cleaning. The characterization used in this study is the Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX). Based on the results of SEM-EDX, it was shown that the 200 mesh zeolite sample and the zeolite that passed the filter had a non-spherical particle shape and no visible pores on the surface, while the microwave zeolite sample had an aggregate shape and visible pores on the particle surface which were very clear. In addition, in the 200 mesh zeolite sample, filtered zeolite and microwave zeolite each had an Al content percentage of 1.64%, 3.18 and 3.80% and a Si content of 7.58%, 15.15% and 18 .38%.

Introduction

Zeolite comes from the Greek words "zeo" (to boil) and "lithos" (stone) which means when zeolite is heated it will quickly boil and lose its water content quickly (evaporate). Zeolite has high water absorption properties and easily releases it when heated [1]. Zeolite is a hydrated alumina-silica mineral formed from tetrahedral alumina (AlO_4^{5-}) and silica (SiO_4^{4-}) with a 3-dimensional crystal structure [2-3].The 3-dimensional structure of zeolite has open cavities consisting of coordination of aluminum, silicon and oxygen with active metals [4]. These cavities also contain metal cations that can be exchanged (ion exchangers) such as K^+, Mg^{2+}, Na^+ and Ca^{2+} [5-6].

Generally, there are two types of zeolite, namely natural zeolite and synthetic zeolite [7]. Natural zeolite has hydrothermal properties and most of the natural zeolite comes from volcanoes, for example clinoptitolite, mordenite, chabazite and others [8]. Synthetic zeolite, of course, comes from processing natural materials or synthetic silicates in the laboratory by imitating the hydrothermal process, namely using high pressure and temperature. Examples of synthetic zeolite are zeolite A, zeolite P, zeolite X, zeolite Y and others [9]. Zeolite has various properties, namely in the form of a Si/Al molar ratio (SiO_2/Al_2O_3) such as hydrophobicity and acid resistivity will increase with the value of the Si/Al molar ratio. Based on the Si/Al molar ratio, zeolite is classified into three types namely low silica zeolite (Si/Al ≤ 2), medium silica zeolite (2 < Si/Al <5) and high silica zeolite (Si/Al ≥ 5) [10] . Low silica zeolite is commonly used to remove ammonium and heavy metals in water because it has a very good ion exchange capacity, whereas high silica zeolite can be used to remove organic contaminants because it has a higher level of hydrophobicity than low silica zeolite [11]. Chemically, zeolite has a general equation, namely:

$$M_{2/n} * Al_2O_3 * SiO_2 * yH_2O \tag{1}$$

where M is a basic cation, n is the valence of the cation, x is the number of Si tetrahedral ($2 \leq x < 10$) and y is the number of water molecules in the zeolite cavity [12]. The most common zeolite mineral compositions in nature are clinoptitolite with relatively high content (80% and above).

Clinoptitolite zeolite has a chemical formula structure of $(Na,K)_6(Si_{30}Al_6O_{72})\bullet 20H_2O$ with an Al/Si ratio of 4.0 – 5.7. The structure of the clinoptitolite zeolite is composed of a two-dimensional system of three types of channels, namely two parallel channels, channel A with 10 ring members, and channel B which intersects perpendicularly to channel C (each 8 ring members). In addition, there are major cations located in the cationic site, namely elements Na, Ca, Ba, K, and Mg. This clinoptitolite zeolite can be used to treat heavy metal waste in water, for example Zn and Cu metal waste [13–15]. Furthermore, clinoptitolite zeolite also has a lot of organic impurities or impurities attached to its surface [16]. These impurities can cover the cavities and surface pores of the zeolite so that it can reduce the absorption quality of the zeolite such as the absorption of the adsorbate in the adsorption process. To remove impurities in zeolite, there is one way to overcome this, namely by using sonication and microwaves. This is because sonication uses ultrasonic waves which are able to clean the material from impurities attached to its surface without damaging its structure while heating in a microwave can improve the structure of the material and produce a more uniform particle size distribution [17]. Furthermore, cleaning zeolite by sonication and microwave can increase the pores in the zeolite because the impurities or impurities attached to the surface of the material are decreasing, so the more repetitions of the sonication and microwave treatment, the higher the purity of the zeolite from impurities [18]. Therefore, this research will be carried out to clean impurities and impurities in clinoptitolite zeolite by sonication and microwave methods.

Experimental Method

The material used in this study was clinoptitolite zeolite from PT Sari Mas Indonesia in Medan City. Illustration of the clinoptitolite zeolite cleaning process can be seen in Figure 1.

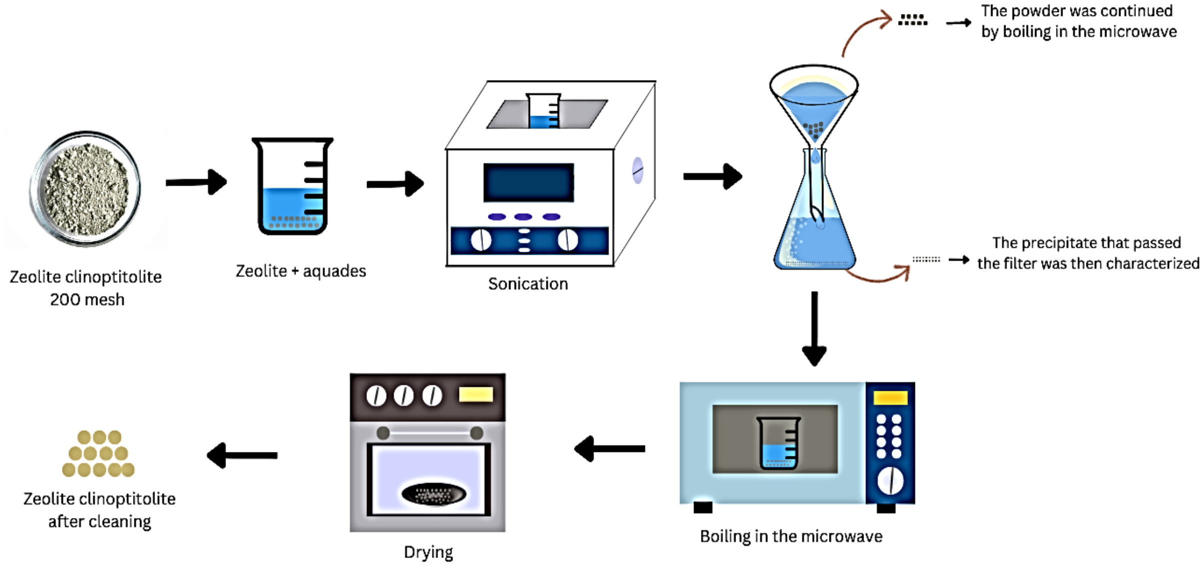


Figure 1. Clinoptitolite zeolite cleaning process

Previously, zeolite was sieved using a 200 mesh sieve. A total of 10 grams of zeolite was mixed into 120.5 ml of distilled water (1:12.5 (w/v)). Sonicate the zeolite solution 10 times, every 1 cycle of sonication was carried out for 15 minutes then followed by rinsing 3 times using filter paper. Take the translucent filtrate from the filter paper where the filtrate still contains fine particles that pass the filter and then stored for characterization. After sonication, the zeolite is boiled in a microwave with low power (100 watts) for 30 minutes, the ratio of zeolite and distilled water is 1:10 b/v. Discard the zeolite cooking water and replace it with fresh distilled water and then boil again. Boil the zeolite in the microwave 10 times. The boiled zeolite is then dried in an oven at 100^{o}C for 24 hours. The characterization used in this study is the Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) Hitachi SU-3500 type. SEM-EDX aims to determine changes in morphology, particle size and elemental content in the sample.

Result and Discussion

Based on the SEM results, the morphology of the 200 mesh zeolite (CZ-200), filter pass zeolite (CZ-F) and clean zeolite (ZC-C) samples can be seen in Figure 2.

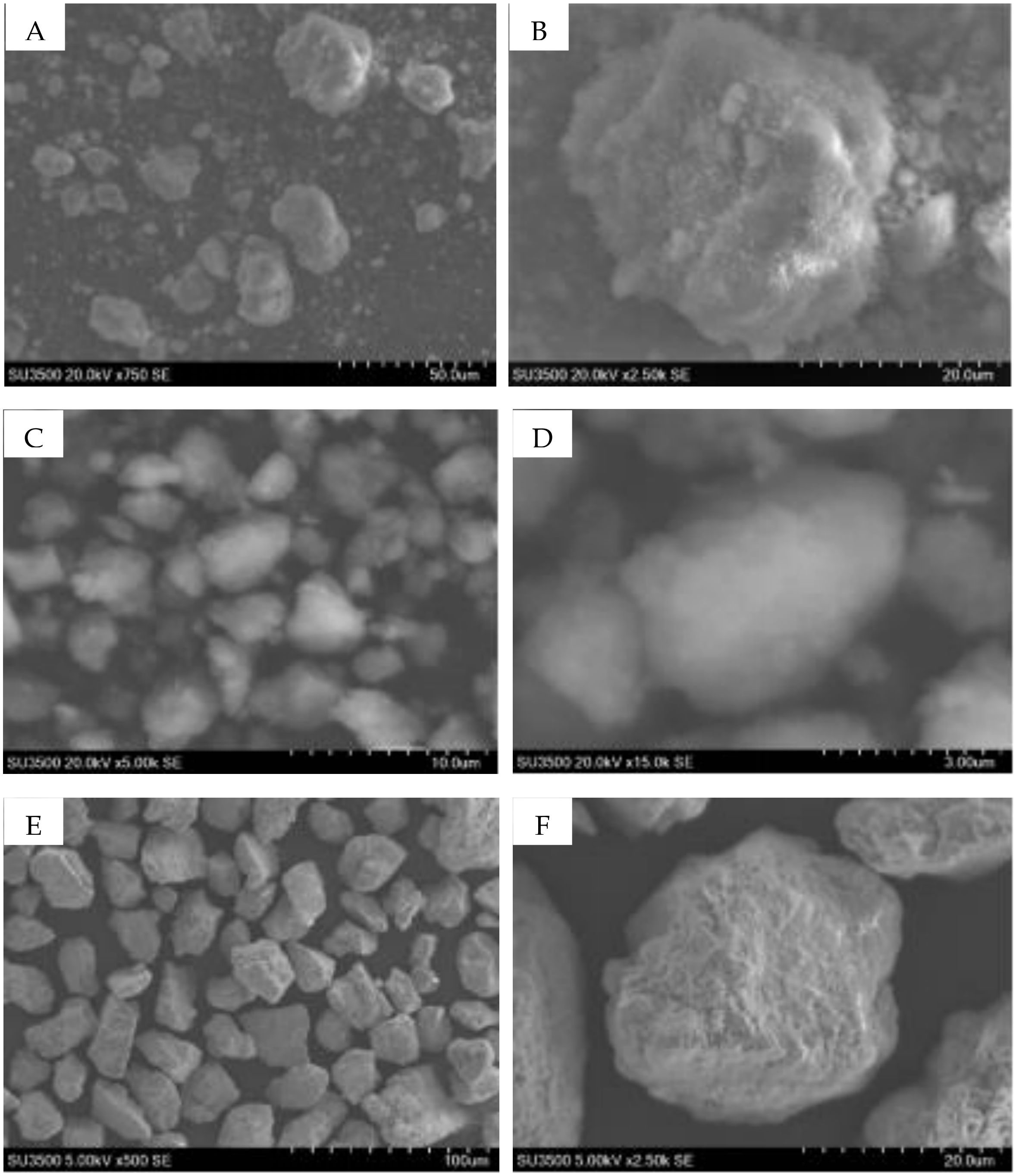
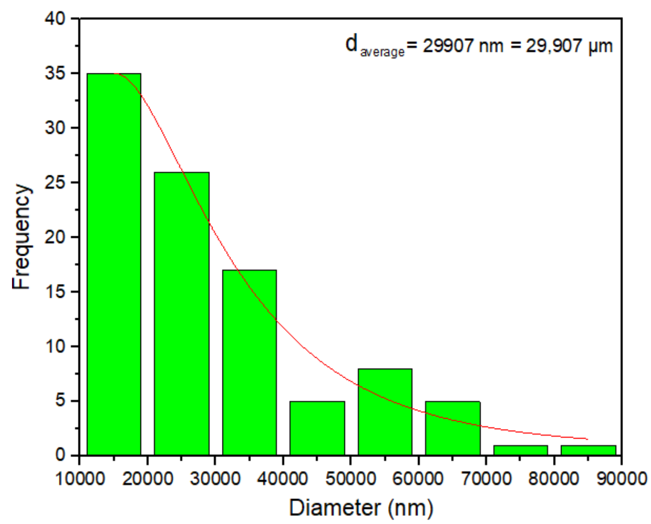
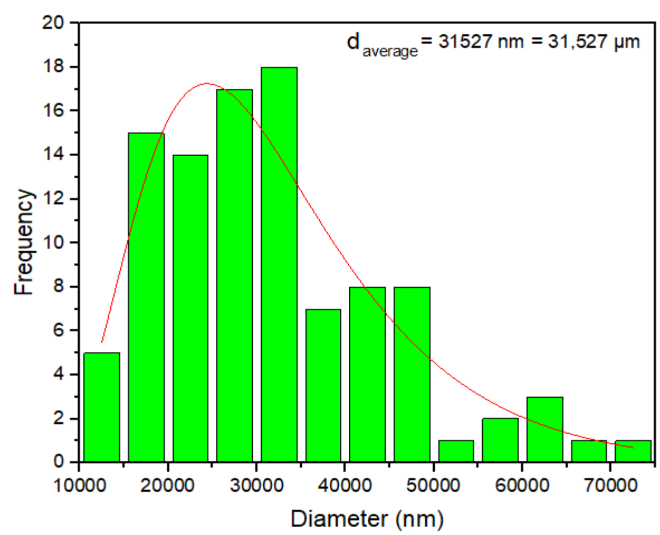


Figure 2. The morphology of the CZ-200 sample (a) 750 times magnification and (b) 2,500 times magnification, the CZ-F sample (c) 5,000 times magnification and (d) 15,000 times and CZ-C (e) 500 times magnification and (f) 2,500 times magnification.

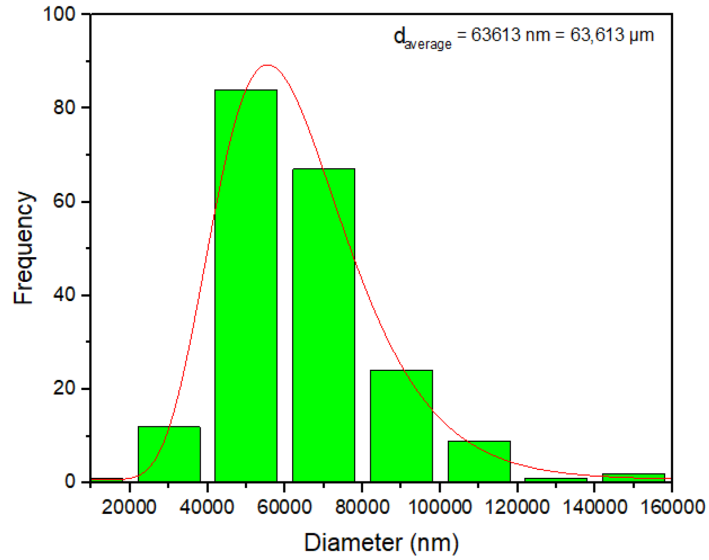
From Figure 2, it can be seen that there are differences in morphological conditions in the CZ-200, CZ-F and CZ-C samples. Figures 3a and 3b show a 200 mesh zeolite sample with a magnification of 750 times and 2,500 times. For a magnification of 750 times it shows that the particles have a non-spherical size while for a magnification of 2500 times it shows that the surface of the particles is not smooth and there are no visible surface pores on the zeolite, this is because the pores on the surface of the zeolite are covered by organic or oxide impurities. free adhering to the surface of the particles and water molecules contained in the zeolite pores [19]. Figures 3c and 3d show zeolite samples that passed the filter with magnifications of 5,000 times and 15,000 times, at this magnification they show a non-spherical particle shape and have a smooth surface but the pores on the surface are still covered by organic impurities and water molecules. Figures 3e and 3f show clean zeolite samples that have been microwaved at magnifications of 500 times and 2,500 times. For a magnification of 500 times, it can be seen that the particles are not round and form aggregates. However, at a magnification of 2,500 times, the surface of the zeolite particles is clean and the pores are very clear. This can be caused by the loss of organic impurities or water content that is located in the pores so that the pore size of the zeolite surface becomes larger. In addition, the use of microwaves on zeolite can increase the surface area of zeolite [20]. Furthermore, the particle size distribution in the sample can be seen in Figure 3.



(a)



(b)

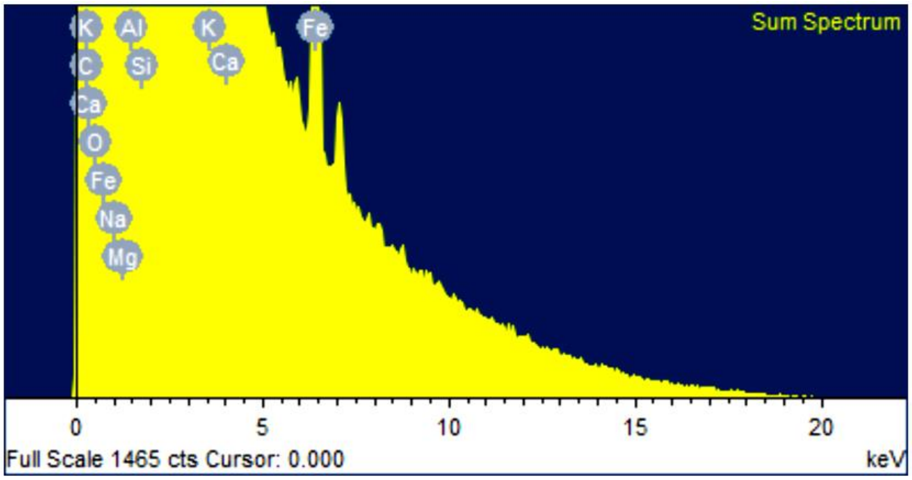


(c)

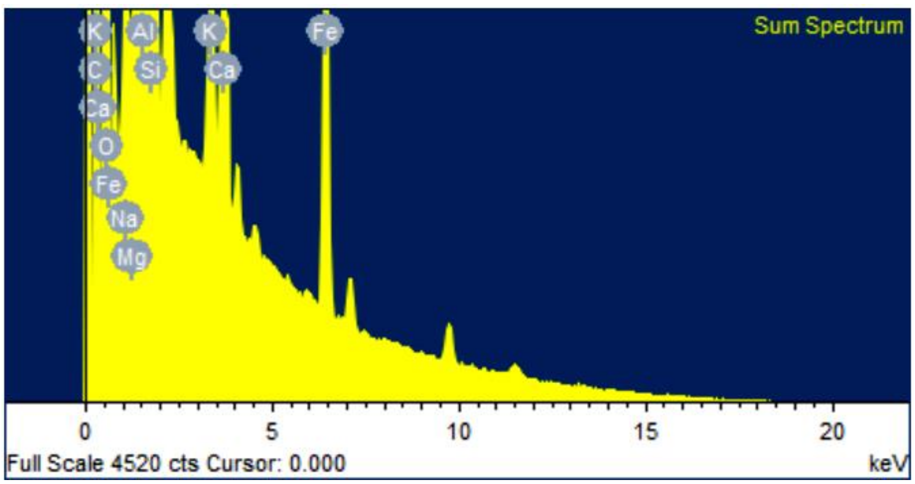
Figure 3. Particle size distribution (a) CZ-200, (b) CZ-F and (c) CZ-C

From Figure 3 it can be seen that there are differences in particle size in the CZ-200 sample, CZ-F and CZ-C. Figure 3a shows the particle size distribution of the 200 mesh zeolite sample. In general, the size of 200 mesh is equal to 74 µm [21], but the particle size in this sample ranges from 11 – 86 µm with an average particle size of 29,907 µm. Particle sizes that exceed 74 µm may be due to the non-uniform cavities in the 200 mesh cockerel so that large particle sizes can also pass through the chicken. In Figure 3b, the particle size distribution in the zeolite samples passing through the sieve ranges from 13 – 70 µm with an average particle size of 31,527 µm. The large size of the zeolite that passes the filter during the washing process is suspected that the particles in the sample stick together during the drying process and the organic impurities are still attached to the sample. Figure 3c shows the particle size distribution of the clean zeolite sample. This sample shows particle sizes ranging from 19 –149 µm with an average particle size of 63,613 µm. It can be seen that the zeolite that has been cleaned with sonication and microwave produces a larger size than the sample before cleaning. The large size is probably due to the sample not fading after drying, where the dried sample will cause the particles to stick together.

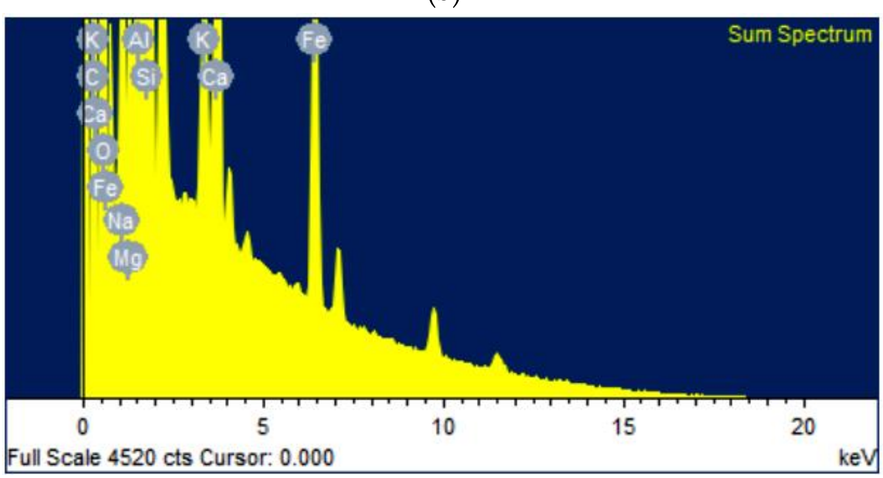
Furthermore, to find out the elements contained in the CZ-200 sample, CZ-F and CZ-C can be seen in Figure 4.



(a)



(b)



(c)

Figure 4. Elemental content of (a) CZ-200, (b) CZ-F and (c) CZ-C.

Figure 4 shows the elements contained in the CZ-200 sample, CZ-F and CZ-C where the percentage value of the element content in more detail can be seen in Table 1.

Table 1. Elemental content in CZ-200, CZ-F and CZ-C.

Sample	%Weightpercent							
	O	Na	Mg	Al	Si	K	Ca	Fe
CZ-200	44,90	0,52	0,13	1,64	7,58	0,52	0,35	0,61
CZ-F	50,52	0,77	0,26	3,18	15,15	1,01	0,68	1,44
CZ-C	49,29	0,81	0,29	3,80	18,38	1,41	0,97	2,60

Based on Table 1, the percentage of elemental weight in CZ-200 samples, CZ-F and CZ-C samples is shown. In the CZ-200 sample and the CZ-F, it showed that the percentage of the largest element content was O element of 44.90% and 50.52%, while for Al element it had a percentage of 1.64% and 3.18% while the Si element was 7.58 % and 15.15%. The low percentage of Al and Si elements is probably due to the large number of organic impurities attached to the zeolite particles. In addition, the percentage of CZ-F is higher than CZ-200 because organic impurities begin to decrease in the zeolite particles caused by the zeolite rinsing process. In the CZ-C sample, the percentage values for the elements O, Al and Si were 49.29%, 3.80% and 18.38%, respectively. From this, it can be seen that there was an increase in the percentage of elements, namely zeolite, before and after cleaning using a microwave. The increase in elemental content is due to the disappearance of organic impurities attached to the surface of the zeolite after cleaning using a microwave so that the Al and Si elements increase and the pore size becomes larger. Furthermore, from the three samples it can be seen that the percentage of Si content is greater than Al which indicates the sample has high hydrophobicity so that it can be applied as an adsorbent to adsorb organic pollutants in water [11].

Conclusion

Analysis of the morphology, elemental content and physical properties of CZ-200, CZ-F and CZ-C samples has been completed. The CZ-200 and CZ-F samples had non-spherical particle shapes with an average particle size of 29.907 μm and 31.527 μm respectively and no visible pores on the surface were caused by organic impurities still attached to the surface. While the CZ-C samples have aggregate-like particle shapes with an average particle size of 63.613 μm and the pores on the surface are clearly visible because organic impurities have been removed during the cleaning process using the sonication and microwave. In addition, the sample has high hydrophobicity where the elemental content of Si (18.38%) is higher than Al (3.80%) so that it can be applied as an adsorbent to treat organic pollutants in water. Furthermore, it is recommended that CZ-200 samples use a sieve that has a uniform diameter to produce a size ≤ 74 μm and for CZ-F and CZ-C it is recommended to grind after the drying process so that the dry samples, the particles do not stick together resulting in a smaller particle size get bigger.

Acknowledgment

The author would like to thank the Department of Physics, Faculty of Mathematics and Natural Sciences at the Postgraduate Program, Sriwijaya University, for providing the opportunity to conduct a Master's Final Assignment (Thesis) research at the Center for Advanced Materials Research (PRMM)-BRIN.

References

[1] M. Moshoeshoe, M. Silas Nadiye-Tabbiruka, and V. Obuseng, “A Review of the Chemistry, Structure, Properties and Applications of Zeolites,” *Am. J. Mater. Sci.*, vol. 2017, no. 5, pp. 196–221, 2017, doi: 10.5923/j.materials.20170705.12.

[2] Y. Setiawan and F. W. Mahatmanti, “Preparasi dan Karakterisasi Nanozeolit dari Zeolit Alam Gunungkidul dengan Metode Top-Down,” *Indones. J. Chem. Sci.*, vol. 7, no. 1, pp. 43–49, 2018.

[3] A. Mastinu *et al.*, “Zeolite clinoptilolite: Therapeutic virtues of an ancient mineral,” *Molecules*, vol. 24, no. 8, 2019, doi: 10.3390/molecules24081517.

[4] N. M. Orjioke, “Synthesis and Characterization of Zeolite and Its Application in Adsorption of Nickel from Aqueous Solution,” *J. Pharm. Chem. Biol. Sci.*, vol. 3, no. 4, pp. 592–600, 2016, [Online]. Available: https://www.jpcbs.info/2015_3_4_19_Orjioke.pdf

[5] S. K. Pavelić, J. S. Medica, D. Gumbarević, A. Filošević, N. Pržulj, and K. Pavelić, “Critical review on zeolite clinoptilolite safety and medical applications in vivo,” *Front. Pharmacol.*, vol. 9, no. NOV, pp. 1–15, 2018, doi: 10.3389/fphar.2018.01350.

[6] R. Kaviani, “Investigation of the Application of Zeolites in the Adsorption Mechanism Investigation of the Application of Zeolites in the Adsorption Mechanism,” *J. Chem. Lett.*, vol. 3, no. May, 2022, doi: 10.22034/JCHEMLETT.2022.338590.1068.

[7] M. Rilyanti, E. Gita Silviana, B. Buhani, K. D. Pandiangan, and N. Luh Gede Ratna Juliasih, “Sintesis Dan Karakterisasi Zeolit Mordenit (Mor) Pori Hirarki Berbasis Silika Abu Ampas Tebu,” *Anal. Environ. Chem.*, vol. 5, no. 02, pp. 178–191, 2020, doi: 10.23960/aec.v5.i2.2020.p178-191.

[8] M. Krol, “Natural vs. Synthetic Zeolites,” *Crystals*, vol. 10, no. 622, pp. 1–8, 2020.

[9] A. Khaleque *et al.*, “Zeolite synthesis from low-cost materials and environmental applications: A review,” *Environ. Adv.*, vol. 2, no. August, 2020, doi: 10.1016/j.envadv.2020.100019.

[10] G. Hu *et al.*, “Recent developments and challenges in zeolite-based composite photocatalysts for environmental applications,” *Chem. Eng. J.*, vol. 417, no. February, p. 129209, 2021, doi: 10.1016/j.cej.2021.129209.

[11] N. Jiang, R. Shang, S. G. J. Heijman, and L. C. Rietveld, “High-silica zeolites for adsorption of organic micro-pollutants in water treatment: A review,” *Water Res.*, vol. 144, pp. 145–161, 2018, doi: 10.1016/j.watres.2018.07.017.

[12] C. Finocchiaro *et al.*, “In situ and micro-Raman spectroscopy for the identification of natural Sicilian zeolites,” *J. Raman Spectrosc.*, vol. 53, no. 3, pp. 525–539, 2022, doi: 10.1002/jrs.6278.

[13] Y. Akdeniz and S. Ülkü, "Microwave effect on ion-exchange and structure of clinoptilolite," *J. Porous Mater.*, vol. 14, no. 1, pp. 55–60, 2007, doi: 10.1007/s10934-006-9008-z.

[14] E. M. Dewi, . Suwardi, D. T. Suryaningtyas, and S. Anwar, "Utilization of Natural Zeolites as Cu (Ii) and Zn (Ii) Adsorbent," *J. Tanah Trop. (Journal Trop. Soils)*, vol. 21, no. 3, p. 153, 2016, doi: 10.5400/jts.v21i3.2203.

[15] B. Bogdanov, D. Georgiev, K. Angelova, I. Markovska, and Y. Hristov, "Natural Zeolites : Clinoptitolite Review," *Int. Sci. Conf. 4th - 5th June 2009, Stara Zagor. Bulg. "Economics Soc. Dev. Base Knowledge,"* vol. VII, no. June, pp. 1–5, 2009.

[16] S. W. Pratomo, F. W. Mahatmanti, and T. Sulistyaningsih, "Pemanfaatan Zeolit Alam Teraktivasi H_3PO_4 sebagai Adsorben Ion Logam Cd(II) dalam Larutan," *Indones. J. Chem. Sci.*, vol. 6, no. 2, pp. 161–167, 2017.

[17] W. W. Purwanto, S. S. Paramitha, D. T. Kimia, F. Teknik, and U. Indonesia, "Ultrasonic and Microwave Application for Purifying Carbon Nanotubes Synthesized By Methane Decomposition Method," *J. Purifikasi*, vol. 12, no. 1, pp. 75–82, 2011.

[18] M. R. Silva *et al.*, "Graphene-oxide loading on natural zeolite particles for enhancement of adsorption properties," *RSC Adv.*, vol. 10, no. 8, pp. 4589–4597, 2020, doi: 10.1039/c9ra00572b.

[19] A. M. Fuadi, M. Musthofa, K. Harismah, Haryanto, and N. Hidayati, "Pemakaian Microwave untuk Optimasi Pembuatan Zeolit Sintetis dari Abu Sekam Padi," *Simp. Nas. Teknol. Terap.*, no. ISSN 2339-028X, pp. 1–5, 2013.

[20] H. I. Umam and T. Hernawati, "Pengaruh Pemanasan Microwave terhadap Morfologi dan Luas Permukaan Material Zeolite NaX," *J. Ind. Manuf.*, vol. 3, no. 1, pp. 11–14, 2018, doi: 10.31000/jim.v3i1.614.

[21] M. Mahardika, H. Abral, A. Kasim, S. Arief, and M. Asrofi, "FTIR and Moisture Absorption of Yam Bean Starch Biocomposites with Yam Bean (Pachyrhizus erosus) Bagasse Fibers as Reinforcement," *J. ILMU DASAR*, vol. 19, no. 2, p. 93, 2018, doi: 10.19184/jid.v19i2.7255.