Walisongo Journal of Chemistry
Walisongo Journal of Chemistry Vol. 6 Issue 1 (2023), 31-37
ISSN: 2621-5985 (online); 2549-385X (print)
DOI: https://doi.org/10.21580/wjc.v6i1.14908

Characterization of Natural Clay from Tulungagung Regency, East Java Province, Indonesia

Mike Rahayu[1*], Novia Amalia Sholeha[2], Siti Rahmah[3,4]

[1]Department of Chemistry Education, Faculty of Tarbiyah and Teacher Training, Universitas Islam Negeri Sayyid Ali Rahmatullah Tulungagung, Jl. Mayor Sujadi No.46, Tulungagung, East Java, 66221, Indonesia
[2]School of Vocational Studies, Bogor Agricultural University (IPB University), Jalan Kumbang No. 14, Bogor 16151, Indonesia
[3]Chemistry Department, Faculty of Mathematics and Natural Science, Universitas Negeri Medan, Jl. Willem Iskandar Psr V Medan Estate, Medan, Indonesia
[4]Chemical Engineering Department, Graduate School of Engineering, Tohoku University, 6-604, Aramaki Aza Aoba Aoba-ku, Sendai, Miyagi 980-8579, Japan

*Corresponding author: mike.rahayu@uinsatu.ac.id

Received: 27 February 2023; Accepted: 20 July 2023; Published: 25 July 2023

Abstract

Natural clay is a material that has various benefits and is abundant in the environment. This research will study about the characteristics of natural clay from Tulungagung, East Java, Indonesia. This research used two samples of Natural Clay-1 (NC-1) and Natural Clay 2 (NC-2) from Tulungagung, Sidem village, Gondang district. The natural clays were dried at room temperature for 2 days then pulverized and sieved using 100 mesh sieves. X-ray diffraction (XRD), x-ray fluorescence (XRF), infrared spectroscopy (IR), and scanning electron microscopy (SEM) have been utilized to characterize the natural clay. XRF analysis revealed that the primary components of Tulungagung's natural clay are Fe, Si, and Al. Montmorillonite, quartz, and anatase are the primary natural clay minerals, as determined by XRD and FTIR. The results of the SEM indicate a non-uniform material surface.

Keywords: *Natural clay; chemical composition; mineral content; morphology*

Introduction

Tulungagung is one of the districts in East Java where most of its territory consists of natural clay. The clay is mostly used as material for bricks and tiles, so it has low economic value. Clay is one of the inorganic materials that has a layered structure which causes clay to have the ability to exchange ion in its layers. Meanwhile clay has many potentials to be used as smart material. Some research showed that clay has been used slow-release agents in fertilizer (Eddarai et al., 2022), catalyst (Baloyi et al., 2018), adsorbent of heavy metal (Gu et al., 2019; Tahya et al., 2022; Uddin, 2017; Zhao et al., 2015) adsorbent of dye waste (Karelius & Asi, 2018b) and hard water desalination (Musawwa et al., 2022).

Clay is a natural mineral that the particle size is less than 2 mm and has a layer of negative charge. Clay is a mineral known as

Copyright © 2023 WJC | ISSN 2621-5985 (online) | ISSN 2549-385X (print)

a mineral that has good adsorption ability. Most clay have arrangements of tetrahedral silica and octahedral aluminum. In tetrahedral silica, a silica atom surrounded by four oxygen atoms at each corner of tetrahedral. While in octahedral aluminum, an aluminum atom surrounded by hydroxyl groups at six corners to form an octahedral structure (Huggett, 2015). The silica and aluminum atoms in clay can be partially replaced by other element called the isomorphic process. The units will form a combination of arrangement to form a clay. The characteristic of each type of clay are influenced by the combination of different basic composition (Darwanto et al., 2019)

Clays are classified based on their mineral content and lattice shape. Based on the lattice shape, clay is divided into two types, namely 1:1 lattice type and 2:1 lattice type which is a ratio of silica-tetrahedral plates and aluminate-octahedral plates. Based on the mineral content, clay is grouped into montmorillonite, kaolinite, haloisite, and illite. Montmorillonite is a clay mineral with the general formula $(OH)_4Si_8Al_4O_{20}.nH_2O$ where nH_2O is water between layers with units of 1: 2. The bond between layers is mainly caused by Van der Waals forces, therefore it is very weak. Kaolinite structural unit consists of layers of silica tetrahedral alternating with octahedral alumina units with a 1:1 lattice type, with the general formula $(OH)_8Al_4Si_4O_{10}$. The mineral kaolinite is stable, and water cannot enter between its plates to cause expansion or contraction in the unit cells. Other minerals from the kaolinite family are haloisite, and Illit, which first encountered in Illinois with the molecular formula $(OH)_4Ky(Si_{8-y}.Al_y)(Al_4.Mg_6.Fe_4.Fe_6)O_{20}$ where y is between 1 and 1.5. The illite clay mineral consists of an octahedral aluminum layer sandwiched between two silica tetrahedral layers (Darwanto et al., 2019).

Every region in Indonesia has different composition of the natural clay. The main component of clay in District Tanah Miring Merauke are quartz, illite, nordstrandite, hematite, and osbornite, and has high crystallinity (Darwanto et al., 2019). The main component of natural clay from Gowa, South Sulawesi are Fe_2O_3, Al_2O_3, and SiO_2, while the main mineral components are quartz, kaolinite, and hematite (Side & Putri, 2022). XRD result of natural clay from Bojonegoro, East Java showed that it consists of kaolin, quartz, and feldspar minerals (Setyaningrum et al., 2021). While the main mineral components of natural clay in Gema village, Kampar, Riau Province consists of quartz, montmorillonite, and kaolinite (Yanti & Muhktar, 2015).

Thus, this paper aims to contribute to characterizing the natural clay in Tulungagung. This paper will study the physical and chemical properties of clay. This paper also can be used as information of utilization of natural clay from Tulungagung to be used to maximize its potential and have higher economic value.

Methods

Material

Glassware (pyrex), pestle mortar, 100 mesh sieves. Sample used was natural clay from Sidem Village, Gondang, Tulungagung.

Preparation of Natural Clay

Natural clay from two different location in Sidem Village were dried at room temperature for 2 days then pulverized and sieved using 100 mesh sieves. The result of the sieve was called NC-1 (Natural Clay 1) and NC-2 (Natural Clay 2). NC-1 was taken from location latitude: S 8°4'9,81516" and longitude: E 111°48'17,92152", while NC-2 was taken from altitude S 8°4'10,95492" and latitude E 111°48'18,1998.

Natural Clay Characterization

The characterization tools used were X-Ray Diffraction (PANanalytical X'pert PRO), XRF (PANanalytical Minipal 4), IR Spectrometer (Shimadzu IR Prestige 21), and SEM (FEI Inspect-S50).

Copyright © 2023 WJC | ISSN 2621-5985 (online) | ISSN 2549-385X (print)

Results and Discussion

The Physical Character of Natural Clay

In this study, natural clay was obtained in the form of fine brown powder. NC-1 is reddish brown, while NC-2 is brown. The picture of natural clay can be seen in Figure 1. The natural clay was taken from two different points in Sidem Village. The color difference of physical appearance in Tulungagung natural clay was due to the solid Fe oxides content. Fe content was also determined by weathering process (Schwertmann, 1988) and their distribution in soil (Jackson, 1957). This result will be confirmed by the XRF characterization result below.

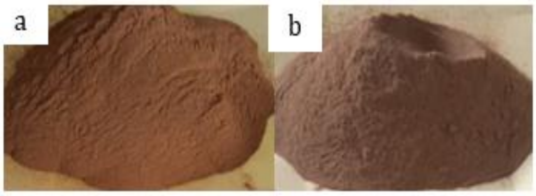

Figure 1. (a) NC- 1, (b) NC-2

XRF Characterization

The chemical composition of the natural clay from Tulungagung was tested using XRF instrument. The result can be seen in Table 1. From Table 1, it can be identified that both NC-1 and NC-2 have main component Fe, Si, and followed by Al elements. The high content of Fe is usually found in natural clay and similar with previous study (Side & Putri, 2022).

The percentage of minerals content is not significantly different. The slight difference of Fe causes the difference in color of NC-1 and NC-2. NC-1 is more reddish than NC-2 because the number of Fe is higher than NC-2. Fe Solid content affect the color of the natural clay (Jackson, 1957).

Table 1. Characterization Result Using XRF

Elements	Percentage (%)	
	NC 1	NC 2
Al	14	13
Si	26.40	28.70
K	0.60	0.98
Ca	2.59	3.20
Ti	2.21	2.23
V	0.14	0.12
Cr	0.08	0.07
Mn	1.00	0.98
Fe	52.60	49.22
Cu	0.22	0.19
Zn	0.07	0.07

XRD Characterization

XRD instrument was used to find the information about the mineral contained, crystallinity and crystal structure. From XRD diffractogram can be seen mineral inside using the specific 2Ɵ peaks. High and sharp peaks indicate that the material has good crystallinity and regularity, whereas broad peaks indicate an amorphous structure. The XRD result is presented in Figure 2.

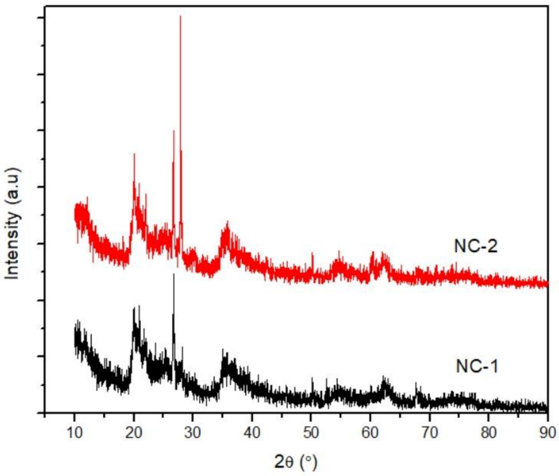

Figure 2. XRD Diffractograms of NC-1 and NC-2

Copyright © 2023 WJC | ISSN 2621-5985 (online) | ISSN 2549-385X (print)

Based on the standard issued by the Joint Committee on Powder Diffraction (JCPDS) number 00-046-1045, the XRD result identified that both NC-1 and NC-2 have the same minerals content. Based on the JCPDS data, the main mineral was quartz (Assila et al., 2020; Yanti & Muhktar, 2015). The main peaks can be seen at 2Ɵ equal to 20.9, 26.6, 29.3, and 36.4. Other minerals that can be found were montmorillonites and anatase. The crystallinity of the material was low because the peaks was broad. The Fe phase was found in 2Ɵ=27.95° in high density due to their presences as impurities.

FTIR Characterization

The purpose of this characterization is to determine the functional group in natural clay from Tulungagung. The FTIR spectra of NC-1 and NC-2 are presented in Figure 3.

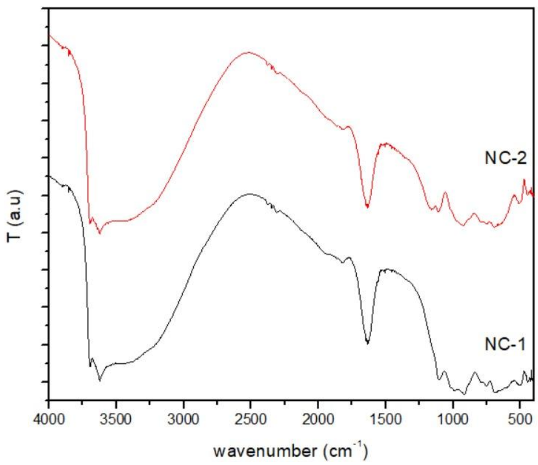

Figure 3. FTIR Spectra of NC-1 and NC-2

The characterization result using FTIR spectrometer for NC-1 and NC-2 showed similar results as shown in Figure 3. have similar spectra. The spectra show that there are several absorption peaks that are quite sharp in wave numbers 3696, 1629, 1002, 910, 798, 753, 677 and 568 cm^{-1} on NC-1, and 3697, 1631, 996, 904, 796, 757, 673, and 578 cm^{-1} on NC-2. The wavelength regions of 1629 and 1631 cm^{-1} are stretching vibrations and bending vibrations of O-H bonds of molecules trapped in the clay crystal lattice (Sadiana et al., 2018). Meanwhile, in the region 3696 and 3697 cm^{-1} show the stretching vibration of -OH bonded to octahedral Al atoms on the silicate surface or inter-layer silicate region of the clay structure. The absorption band correlates with the presence of peak spectra in 1002, 910, 996, 904 cm^{-1} indicating the presence of Al-OH bending vibrations.

The absorption band correlates with the presence of peak spectra in 1002, 910, 996, 904 cm^{-1} indicating the presence of Al-OH bending vibrations. Meanwhile, in the region 3696 and 3697 cm^{-1} show the stretching vibration of -OH bonded to octahedral Al atoms on the silicate surface or inter-layer silicate region of the clay structure. The presence of silicate surface in accordance with the XRD results that the main properties of clays is silicate (SiO_2).

The sharp absorption peaks in the 1002 and 996 cm^{-1} regions indicate the characteristic absorption of Si-O stretching vibrations. The strong absorption in the region 950-1250 cm^{-1} is the stretching vibration of M-O (where M=Si or Al) which involves the principal motion of Oxygen atom in Si-O. This data correlates with the wave numbers in the 673 and 677 cm^{-1} regions which are characteristic of Si-O stretching vibrations. The absorption bands in the 798 and 796 cm^{-1} regions show the stretching vibration of O-Si-O which is characteristic of microcrystalline SiO_2 or quartz (Karelius & Asi, 2018a; Sadiana et al., 2018).

The absorption bands of 753 and 757 cm^{-1} indicate the presence of symmetric vibrations of Si-O-Si in the tetrahedral layer of the clay and the absorption bands in the 568 and 578 cm^{-1} areas indicate the presence of stretching vibrations in $Si\text{-}O\text{-}Al^{VI}$ (Al octahedral). Thus, based on all information obtained, NC-1 and NC-2 contain silica alumina mineral.

SEM Characterization

Scanning Electron Microscope (SEM) is used to examine and analysis the material surface. The SEM result is presented in Figure

Copyright © 2023 WJC | ISSN 2621-5985 (online) | ISSN 2549-385X (print)

4. As revealed by SEM, shows irregularly shaped particles of different sizes. The difference size may be affected by the agglomeration into much larger cluster by the particles of natural clays (Boulahbal et al., 2022). NC-1 and NC-2 have a non-uniform morphology. This is directly proportional to the XRD results which show that those materials do not have sharp peaks and tend to be amorphous.

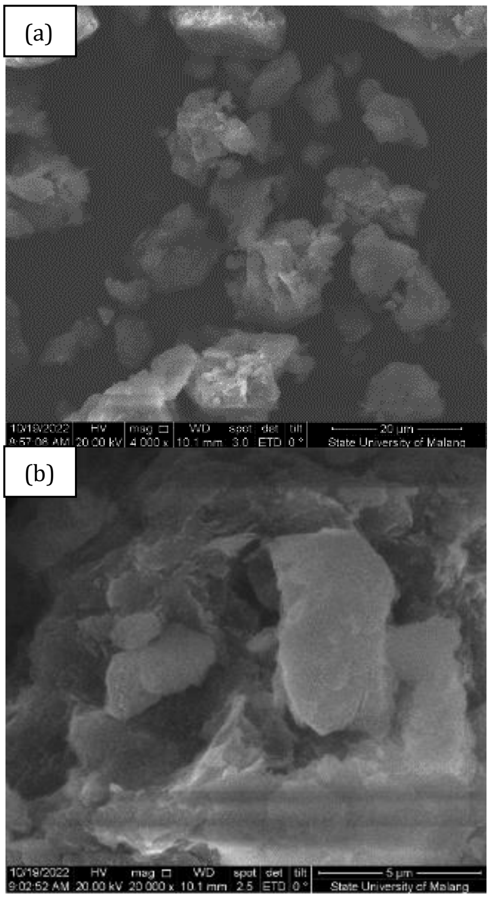

Figure 4. SEM image 20000x (a) NC-1, and (b) NC-2

Based on the characterizations results above, the main component of natural clay from Tulungagung is iron as impurities. Apart from iron, natural clay from Tulungagung contains Si and Al elements. The percentage of Si and Al elements tends to be higher than the Fe element, however, since the ratio of Si:Al, is 2:1, the natural clay of Tulungagung can be used as a source of advanced material such as zeolite X. Zeolite X is a chemical material that has a Si:Al composition ratio of 2:1 (Asfadiyah, 2014). In the future, to reduce the impurities and increase the percentage of elements, the natural clay must be activated first.

Conclusion

This study concludes that quartz is the main phase mineral in natural clay from Tulungagung. Other minerals that can be found were montmorillonites and anatase. The main component of clay is Fe, Si, and Al elements. The crystallinity of the material is amorphous. The presence of peak spectra in 1002, 910, 996, 904, 3696 and 3697 cm^{-1} indicating the presence of silicate surface in accordance with the XRD results in the fact that the main properties of clays are silicate (SiO_2). SEM result shows irregularly shaped particles of different sizes and a non-uniform morphology of NC-1 and NC-2.

Acknowledgement

We would like to thank LP2M UIN Sayyid Ali Rahmatullah for providing research funding from BOPTN number 221140000045975.

Reference

Asfadiyah, N. R. (2014). *Sintesis dan Karakterisasi Zeolit X dari Abu Ampas Tebu dengan Variasi Rasio Molar Si/Al Menggunakan Metode Sol-Gel*. Maulana Malik Ibrahim State Islamic University.

Assila, O., Tanji, K., Zouheir, M., Arrahli, A., Nahali, L., Zerrouq, F., & Kherbeche, A. (2020). Adsorption studies on the removal of textile effluent over two natural eco-friendly adsorbents. *Journal of Chemistry.* vol. 2020, Article ID 6457825, 13 pages, 2020. https://doi.org/10.1155/2020/6457825

Copyright © 2023 WJC | ISSN 2621-5985 (online) | ISSN 2549-385X (print)

Baloyi, J., Ntho, T., & Moma, J. (2018). Synthesis and application of pillared clay heterogeneous catalysts for wastewater treatment: A review. In *RSC Advances* (Vol. 8, Issue 10, pp. 5197–5211). Royal Society of Chemistry. https://doi.org/10.1039/c7ra12924f

Boulahbal, M., Malouki, M. A., Canle, M., Redouane-Salah, Z., Devanesan, S., AlSalhi, M. S., & Berkani, M. (2022). Removal of the industrial azo dye crystal violet using a natural clay: Characterization, kinetic modeling, and RSM optimization. *Chemosphere*, *306*. https://doi.org/10.1016/j.chemosphere.2022.135516

Darwanto, Suwito, & Fatimah, H. (2019). Karakterisasi Lempung Alam Asal Distrik Tanah Miring Kabupaten Merauke sebagai Adsorben Bleaching CPO (Crude Palm Oil). *Avogadro Jurnal Kimia*, *3*(1), 35–42.

Eddarai, E. M., el Mouzahim, M., Boussen, R., Bellaouchou, A., Guenbour, A., & Zarrouk, A. (2022). Chitosan-kaolinite clay composite as durable coating material for slow release NPK fertilizer. *International Journal of Biological Macromolecules*, *195*, 424–432. https://doi.org/10.1016/j.ijbiomac.2021.12.055

Gu, S., Kang, X., Wang, L., Lichtfouse, E., & Wang, C. (2019). Clay mineral adsorbents for heavy metal removal from wastewater: a review. In *Environmental Chemistry Letters* (Vol. 17, Issue 2, pp. 629–654). Springer. https://doi.org/10.1007/s10311-018-0813-9

Huggett, J. M. (2015). Clay Minerals. In *Reference Module in Earth Systems and Environmental Sciences* (pp. 1–8). Elsevier. https://doi.org/10.1016/B978-0-12-409548-9.09519-1

Jackson, M. L. (1957). Frequency Distribution Of Clay Minerals In Major Great Soil Groups As Related to The Factors Of Soil Formation. *Clay and Clays Mineral*, *6*, 133–143.

Karelius, & Asi, N. B. (2018a). Sintesis Dan Karakterisasi Komposit Magnetik Lempung Putih Asal Kalimantan Tengah Sebagai Adsorben Zat Warna Pada Limbah Cair. *Jurnal Ilmiah Kanderang Tingang*, *9*(1), 51–66.

Karelius, & Asi, N. B. (2018b). Sintesis Dan Karakterisasi Komposit Magnetik Lempung Putih Asal Kalimatan Tengah Sebagai Adsorben Zat Warna Pada limbah Cair. *Jurnal Ilmiah Kanderang Tingang*, *9*(1), 51–66.

Musawwa, M. M., Ardiyanto, N. R. N., Lestari, A., Yusuf, A. K., & Solehudin, M. (2022). Synthesis of Zeolite Based Material With Aluminum Sources from Used Beverage Cans for Hard Water Desalination. *Walisongo Journal of Chemistry*, *5*(1), 37–44. https://doi.org/10.21580/wjc.v5i1.9172

Sadiana, I. M., Fatah, A. H., & Karelius. (2018). Aktivasi Dan Karakterisasi Lempung Alam Asal Kalimantan tengah Sebagai Salah Satu Alternatif Bahan Adsorben. *Seminar Nasional Pendidikan*, 216–226.

Schwertmann, U. (1988). Occurence And Formation Of Iron Oxides In Various Pedoenvironments. In *Iron in Soils and Clay Minerals* (pp. 267–308).

Setyaningrum, D., Sujiat, S., & Azizah, A. N. (2021). Characterizayiom Of Clay Materials Used For Pottery Purposes From Rendeng, Malo, Bojonegoro. *Jurnal Neutrino*, *14*(1), 6–11. https://doi.org/10.18860/neu.v14i1.12753

Copyright © 2023 WJC | ISSN 2621-5985 (online) | ISSN 2549-385X (print)

Side, S., & Putri, S. E. (2022). Characterization of Natural Clay from Gowa Regency, South Sulawesi Province, Indonesia. *Jurnal Akademika Kimia*, *11*(2), 72–76. https://doi.org/10.22487/j24775185.2022.v11.i2.pp72-76

Tahya, C. Y., Cornelia, M., Siregar, T. M., & Taipabu, M. I. (2022). Adsorption of Copper Ion from Acidic Wastewater by Local Natural Zeolite. *Walisongo Journal of Chemistry*, *5*(2), 136–144. https://doi.org/10.21580/wjc.v5i2.11714

Uddin, M. K. (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. In *Chemical Engineering Journal* (Vol. 308, pp. 438–462). Elsevier B.V. https://doi.org/10.1016/j.cej.2016.09.029

Yanti, P. H., & Muhktar, D. A. (2015). Karakterisasi Lempung Alam Desa Gema Teraktifasi Fisika. *Chem. Prog*, *8*(1). https://doi.org/10.35799/cp.8.1.2015.9396

Zhao, Y., Qi, W., Chen, G., Ji, M., & Zhang, Z. (2015). Behavior of Cr(VI) removal from wastewater by adsorption onto HCl activated Akadama clay. *Journal of the Taiwan Institute of Chemical Engineers*, *50*, 190–197. https://doi.org/10.1016/j.jtice.2014.12.016

Copyright © 2023 WJC | ISSN 2621-5985 (online) | ISSN 2549-385X (print)