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Characterization of Natural Clay from Gowa Regency, South Sulawesi Province, Indonesia

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Abstract

Clay is one of the essential natural minerals in human life, especially in the industrial sector, which is widely used as a raw material for ceramics fabrication, adsorbents, and photocatalysts. The characteristics of clay significantly affect the quality of the resulting material. This study will study the aspects of natural clay in Gowa Regency, South Sulawesi Province, without the leaching process and with acid leaching. Acid leaching uses 3 M HCl, previously roasted at a temperature of 600 °C. The characterization consisted of metal oxide analysis using XRF, mineral content analysis using XRD, morphological analysis, and compound content using SEM-EDX. The results showed that the primary metal oxide content in natural clay was Fe_2O_3, Al_2O_3, and SiO_2, the content of Fe_2O_3 decreased after the raw clay was treated with acid. The main mineral content in the sample is quartz, kaolinite, and hematite. The sample's morphology looks different after being given acid treatment; the acid leaching natural clay sample shows a porous morphology, while the natural clay without acid leaching shows the morphology in the form of lumps. The EDX mapping analysis showed that the number of impurities decreased after being given acid treatment.

Keywords: Natural clay, mineral content, morphology, acid leaching

Introduction

Indonesia is a country that has abundant natural resource potential. One of them is natural minerals. Among natural minerals, metal oxides are the main content with great potential to be developed as the basis for manufacturing advanced and high-tech materials such as alumina (Al_2O_3) and silica (SiO_2). The most important content of alumina and silica metal oxides is in clay, resulting from chemical weathering (Manjate et al., 2020). Clay is a layered silicate mineral (phyllosilicate) that is plasticity and hardens when heated or dry.

The basic crystal structure of clay minerals consists of one or two layers of silicon dioxide with one sheet of aluminum oxide. In the silica layer, the basic unit is the silica tetrahedron; one silica atom is bonded to four oxygen atoms. If each tetrahedron shares 3 of the other 4 oxygens, it will form a hexagonal structure called a tetrahedral layer. The basic units of alumina are the octahedron and the hydroxide ion. Aluminum atoms are bonded to 6 oxygen atoms, and each octahedron atom shares its 6 oxygen atoms to form a hexagonal structure called an octahedral layer.

Clay is one of the essential minerals because it is used as a primary material in various industries, such as in ceramic fabrication (Putri et al., 2018), as an adsorbent, and as a photocatalyst (Khennaoui et al., 2020). One of the essential things that must be studied before using clay in this application is the mineral content, metal oxides, and characteristics of natural clay. The mineralogy of clay constituents significantly affects the expansive properties of clay (Utami, 2018).

Based on the results before, Kagonbé et al. (2021) studied the mineral content of Cameroon's natural clay minerals, containing smectites, illite, kaolinite, quartz, feldspar, and mica. The metal oxide content consists of SiO_2 (46-55%), Al_2O_3 (19-21%), and Fe_2O_3 (6.58-10.82%). The same study was done by Tsozué et al. (2017), who studied the mineral content and physicochemical natural clay from Maroua Cameroon and reported that the mineral content contained is quartz and feldspar, and plagioclase; the dominant metal oxide content is SiO_2, Al_2O_3, and Fe_2O_3. Putri & Pratiwi (2017) also reported high content of silica (65.39%) and alumina (9.02%), as well as some impurities, contained such as Fe_2O_3 and TiO_2.

Several methods have been used to remove impurities in clay minerals, including acid leaching (Tripathy et al., 2019), alkaline leaching (Li et al., 2019), high pressure (Wu et al., 2012), and high temperature (Bai et al., 2011). High pressure and high-temperature methods also use acid or base

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solutions and some additive compounds. In this study, acid leaching was used to remove impurities contained in natural clay. Furthermore, it will investigate the characteristics of natural clay obtained from the Gowa Regency, South Sulawesi, Indonesia. The clay studied consisted of natural clay without treatment and natural clay with acid leaching treatment.

Methods

Sample preparation

The natural clay was dried first, then pulverized and sieved 60 mesh; the sample used was clay that passed the sieve.

Acid leaching of natural clay

Before leaching the natural clay sample, it was roasted at a temperature of 600 ºC in a furnace using a rate of 10 ºC/min and a hold time of 2 h. The leaching process was carried out using 3 M HCl, stirring for 5 hours at 80 ºC, then filtered and calcined with calcination temperatures of 900 ºC.

Sample characterization

The metal oxide content of natural clay samples was analyzed using XRF Thermo Fischer Scientific with vacuum X-Ray path, eff. stationary 13.0 mm, and eff. area of 132.7 mm^2. X-ray diffraction (XRD) was performed using Rigaku Miniflex II with CuKα radiation (λ = 1.5405 Å) ranging from 15º ≤ 2θ ≤ 80º, and operation at 30 kV and 10 mA. Scanning electron microscopy (SEM) was performed using a JCM-600Plus scanning electron microscope where the electron beam was set to 15 kV.

Results and Discussion

Analysis of metal oxide using XRF

The metal oxide content of natural clay before and after acid treatment was analyzed using XRF; the results obtained are shown in **Table 1**.

Table 1. The metal oxide content on natural clay

Composition	Content (wt.%)	
	Natural clay	Acid leaching natural clay
Fe_2O_3	55.13	47.83
SiO_2	18.30	24.51
Al_2O_3	10.15	16.27
TiO_2	8.43	5.14
K_2O	5.72	3.73
MnO	1.37	1.25
CaO	0.26	0.30
ZrO_2	0.15	0.15
Cr_2O_3	0.19	0.19
CuO	0.09	0.13
SrO	0.08	0.17
ZnO	0.02	0.12
Nb2O5	0.05	0.06
Rb2O	0.04	0.09
Y2O3	0.02	0.06

Based on **Table 1**, the main content in natural clay is Fe_2O_3,·SiO_2, and Al_2O_3. The high content of Fe_2O_3 in this clay is similar to the sample used in the previous study (Yadav & Bhattacharyya, 2020), which uses clay in the form of kaolin and has a relatively high content of Fe_2O_3 and TiO_2. The high content of Fe_2O_3 and TiO_2 in natural clay is supported by data from mineral analysis using XRD (which will be discussed in the next session).

The amount of Fe_2O_3 decreased after the natural clay was acid leached, from 55.13% to 47.83%. It is because the acid leaching treatment aims to reduce the number of impurities in the raw clay (Chen et al., 2020). With the addition of HCl, it is assumed that iron ions will dissolve in acidic solvents to form $FeCl_3$.

Analysis of mineral content using XRD

The mineral content in natural clay was analyzed using XRD. The analysis is shown in **Figure 1**.

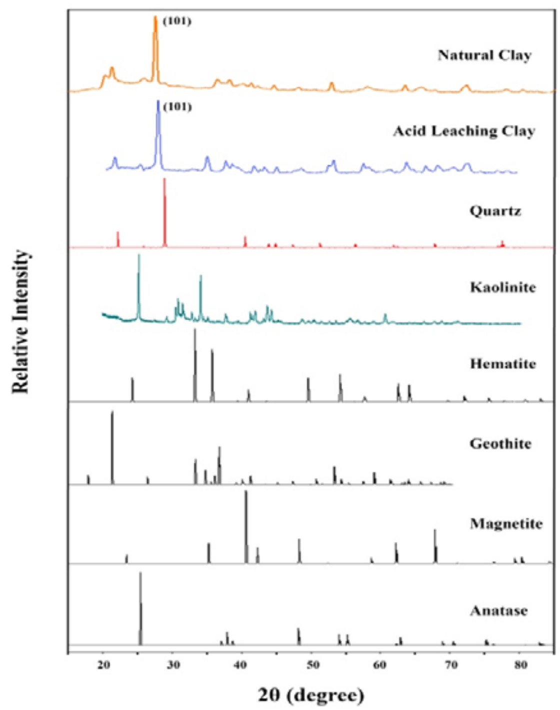

Figure 1. Diffractogram natural clay and acid leaching clay

Based on **Figure 1,** it can be seen that the primary minerals contained in the sample are quartz (SiO_2), kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), and hematite ($Fe_2O_3.H_2O$). Some minerals with not-so-high peaks that are thought to act as impurities are goethite (FeOOH), magnetite (Fe_3O_4), and anatase (TiO_2). This impurity is almost similar to natural clay from Queensland, Australia, where the impurity minerals in the sample consist of minerals derived from metal oxides of iron and titanium (Pepper et al., 2021).

The peaks of hematite, goethite, and magnetite in the acid leaching clay sample are not too sharp, so it can be concluded that the impurities in the acid leaching clay sample have decreased after receiving acid treatment. In addition, the peaks in the acid leaching clay sample were sharper, so this sample was more crystalline than the sample without acid treatment. It is in line with the research results of Ferdowsi et al. (2019), which show a narrowing of the band and a decrease in peak intensity on the diffractogram, indicating a reduction in the number of impurities in the sample.

Analysis morphology using SEM

The morphology of the samples was analyzed using SEM, shown in **Figure 2**. It can be seen that there are differences in the morphology of natural clay samples with an acid treatment and without acid treatment.

The acid-treated samples showed a porous morphology, while the non-acid-treated samples showed a generally dense texture, a unique characteristic of clay minerals.

The appearance of pores in the acid-leaching clay sample indicates the dissolution of some impurities so that the pores on the sample's surface are open. It is in line with the results of Xu et al. (2017), which show the morphological changes in clay samples after treatment.

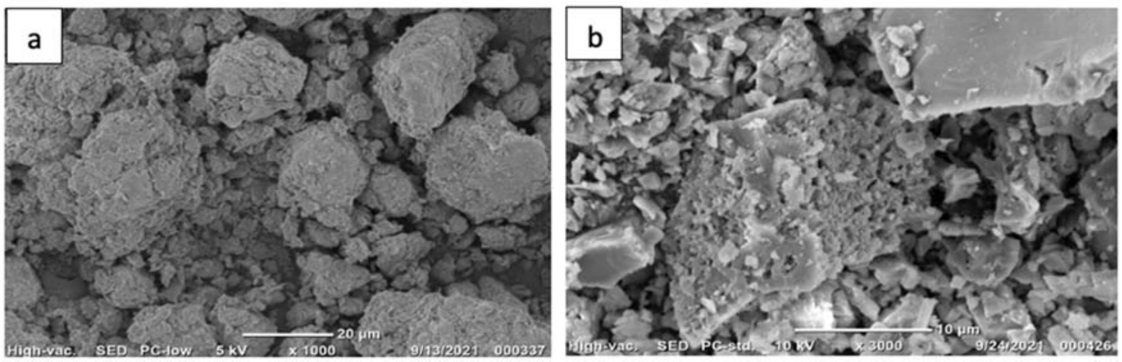

Figure 2. Samples morphology using SEM 5 kV with magnification 1000× (a) natural clay (b) acid leaching clay

EDX and mapping analysis

EDX and mapping analysis was carried out to determine the elemental content in the sample and the pattern of distribution of elements on the sample surface. The results of EDX and mapping analysis are shown in **Figure 3**.

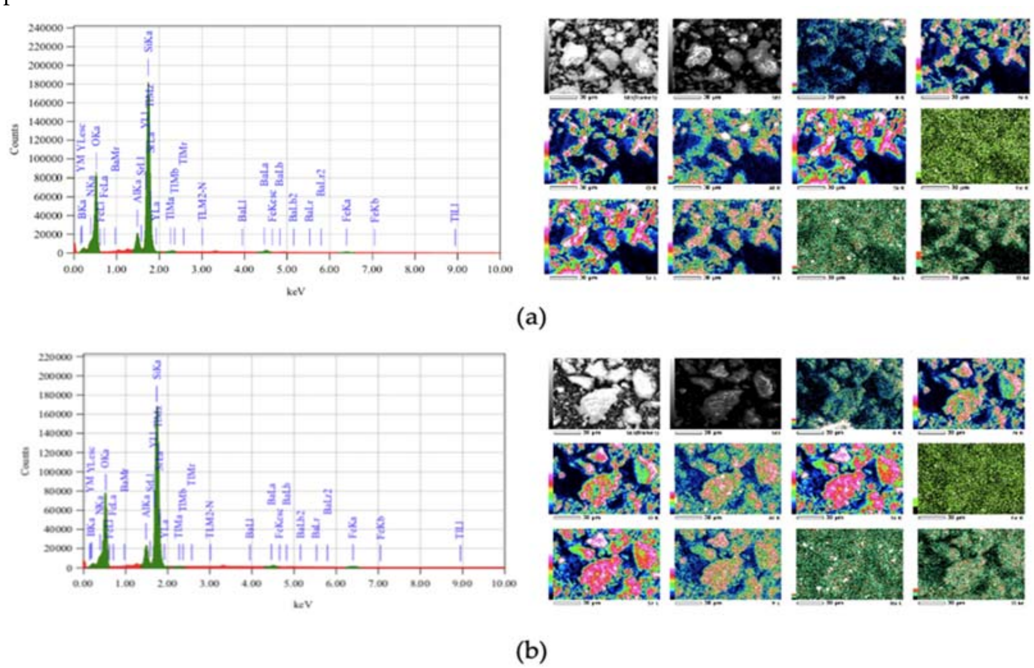

Figure 3. EDS mapping analysis of (a) natural clay and (b) acid leaching natural clay

EDX analysis shows that clay minerals are rich in Fe, Al, and Si. The most significant element in the sample is oxygen. The elements of aluminum and silicon are evenly distributed on the sample's surface. The impurity that is quite visible on the surface is elemental iron.

The results of the interpretation of the EDX analysis in the form of mass, atomic, and mole percentages are shown in **Table 2**. The number of percentages shown from the results of the EDX analysis is different from the results of the XRF analysis; this is presumably because, at the time of analysis using EDX only specific points (Foroutan et al., 2019).

Based on **Table 2**, it is shown that the amount of Fe impurities decreased after being given acid treatment. At the same time, the amount of alumina-silica increased after being given acid treatment. It happens because the composition of impurities has decreased so that quantitatively the number of alumina-silica increases.

Table 2. The percentage of the mass, atom, and mol of natural clay and acid leaching clay, corresponding to EDX analysis

Element	Compound	Mass (%) of element		Atom (%)		Mol (%) of compounds	
		Natural clay	Acid leaching natural clay	Natural clay	Acid leaching natural clay	Natural clay	Acid leaching natural clay
B K	B_2O3	4.77	6.36	10.62	13.98	7.23	11.95
N K	N	0.66	0.66	2.17	1.12	1.96	1.91
O K	-	21.15	21.44	32.71	31.86	-	-
Al K	Al_2O_3	4.50	5.24	3.96	4.62	3.00	3.95
Si K	SiO_2	52.10	53.26	44.67	45.07	60.01	77.05
Fe K	Fe_2O_3	3.49	0.92	1.66	0.39	1.11	0.67
Sr L	SrO	8.53	7.22	3.13	1.96	3.57	3.35
Y L	Y_2O_3	2.69	2.18	0.75	0.58	0.63	0.50
Ba L	BaO	1.35	1.83	0.24	0.32	0.41	0.54
Tl M	Tl_2O_3	0.75	0.89	0.09	0.10	0.08	0.09

Conclusions

The results showed that the primary metal oxide content in natural clay was Fe_2O_3, Al_2O_3, and SiO_2, the content of Fe_2O_3 decreased after the raw clay was given acid treatment, from 55.13% to 47.83% (the result of XRF analysis). The main mineral content in the sample is quartz, kaolinite, and hematite. The morphology of the samples appeared different after being given acid treatment; The acid-treated samples showed a porous morphology while the non-acid-treated samples showed a generally dense texture, a unique characteristic of clay minerals. The EDX mapping analysis showed that the number of impurities decreased after being given acid treatment.

Conflict of Interest

The authors declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Bai, G., Qiao, Y., Shen, B., & Chen, S. (2011). Thermal decomposition of coal fly ash by concentrated sulfuric acid and alumina extraction process based on it. *Fuel Processing Technology*, *92*(6), 1213–1219.

Chen, Z., Zhang, Z., Liu, D., Chi, X., Chen, W., & Chi, R. (2020). Swelling of clay minerals during the leaching process of weathered crust elution-deposited rare earth ores by magnesium salts. *Powder Technology*, *367*(May), 889–900.

Ferdowsi, S., Salem, A., & Salem, S. (2019). Spectrophotometrical analysis for fabrication of pH-independent nano-sized γ-alumina by dealumination of kaolin and precipitation in the presence of surfactant composites. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *218*(July), 109–118.

Foroutan, R., Mohammadi, R., Adeleye, A. S., Farjadfard, S., Esvandi, Z., Arfaeinia, H., Sorial, G. A., Ramavandi, B., & Sahebi, S. (2019). Efficient arsenic(V) removal from contaminated water using natural clay and clay composite adsorbents. *Environmental Science and Pollution Research*, *26*(October), 29748–29762.

Kagonbé, B. P., Tsozué, D., Nzeukou, A. N., & Ngos, S. (2021). Mineralogical, physico-chemical and ceramic properties of clay materials from Sekandé and Gashiga (North, Cameroon) and their suitability in earthenware production. *Heliyon*, *7*(7), 1-10.

Khennaoui, B., Zehani, F., Malouki, M. A., Menacer, R., & López, M. C. (2020). Chemical and physical characterization of a natural clay and its use as photocatalyst for the degradation of the methabenzthiazuron herbicide in water. *Optik*, *219*(October), 165024.

Li, X., Wang, H., Zhou, Q., Qi, T., Liu, G., Peng, Z., & Wang, Y. (2019). Efficient separation of alumina and silica in reduction-roasted kaolin by alkali leaching. *Transactions of Nonferrous Metals Society of China*, *29*(2), 416–423.

Manjate, V. A., Issufo, Z., & Magenge, A. L. (2020). Evaluation of clay soils from manjacazi district (mozambique) as potential raw material for the ceramic industry. *Heliyon*, *6*(10), 1-9

Pepper, R. A., Perenlei, G., Martens, W. N., & Couperthwaite, S. J. (2021). High purity alumina synthesised from iron rich clay through a novel and selective hybrid ammonium alum process. *Hydrometallurgy*, *204*(September), 1-9.

Putri, S. E., & Pratiwi, D. E. (2017). Analisis kandungan mineral dalam tanah liat alam sulawesi selatan sebagai bahan dasar sintesis keramik analysis of mineral in south sulawesi natural clay as basic. *Material of Ceramic Synthesis, 18*(1), *35–38.*

Putri, S. E., Pratiwi, D. E., Tjahjanto, R. T., Mardiana, D., & Subaer. (2018). On the effect of acrylamide and methylenebicacrylamid ratio on gelcasted ceramic pore character. *Journal of Chemical Technology and Metallurgy*, *53*(5), 841–844.

Tripathy, A. K., Behera, B., Aishvarya, V., Sheik, A. R., Dash, B., Sarangi, C. K., Tripathy, B. C., Sanjay, K., & Bhattacharya, I. N. (2019). Sodium fluoride assisted acid leaching of coal fly ash for the extraction of alumina. *Minerals Engineering*, *131*(January), 140–145.

Tsozué, D., Nzeugang, A. N., Mache, J. R., Loweh, S., & Fagel, N. (2017). Mineralogical, physico-chemical and technological characterization of clays from Maroua (Far-North, Cameroon) for use in ceramic bricks production. *Journal of Building Engineering*, *11*(May), 17–24.

Utami, D. N. (2018). Kajian jenis mineralogi lempung dan implikasinya dengan gerakan tanah. *Jurnal Alami: Jurnal Teknologi Reduksi Risiko Bencana*, *2*(2), 89-97.

Wu, C., Yu, H., & Zhang, H. (2012). Extraction of aluminum by pressure acid-leaching method from coal fly ash. *Transactions of Nonferrous Metals Society of China*, *22*(9), 2282–2288.

Xu, G., Feng, Q., Deconinck, J. F., Shen, J., Zhao, T., & Young, A. L. (2017). High-resolution clay mineral and major elemental characterization of a Permian-Triassic terrestrial succession in southwestern China: Diagenetic and paleoclimatic/paleoenvironmental significance. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *481*(September), 77–93.

Yadav, A. K., & Bhattacharyya, S. (2020). A new approach for the fabrication of porous alumina beads using acid leachate of kaolin. *Microporous and Mesoporous Materials, 293*(February), 109795.