The Effect of Mechanical Treatment and Calcination Temperature of Ethiopian Kaolin on Amorphous Metakaolin Product

Tadele Assefa Aragaw(✉)

Faculty of Chemical and Food Engineering, Bahir Dar Institute of Technology,
Bahir Dar University, Bahir Dar, Ethiopia
taaaad82@gmail.com

Abstract. Industrial practice of kaolin minerals reveals physicochemical and mineralogical characteristics which make them very useful in many different applications. Even kaolin is important for industrial applications, the presence of contamination can affect the properties of it. So, it is important to treat and characterize the kaolin for their appropriateness of industrial application. The effect of beneficiation and calcinations methods of treatment on the structure of kaolin was studied using XRD and FTIR for the determination of crystalline structure, functional group identification and the thermogravimetry properties of the kaolin. XRD analysis showed that the crystalline of raw kaolin were reduced via beneficiation and calcinations. The effect of beneficiation and calcinations results shows that improvement to a very high grade with physic-chemical characteristics of metakaolin close to that of ideal kaolin. The XRD results depicted that the characteristics reflection of kaolinite and quartz were as a major peak. The FTIR vibration indicates as the major kaolinite clay functional groups in the mineral. From this study, it can be conclude that the major properties for industrial grade specification significantly increased after a certain treatment process.

Keywords: Thermal treatment · Mechanical treatment · Kaolin · Characterization

1 Introduction

Kaolinite comes into view as stacked pseudo hexagonal platelets with a common brochure like shape. Each layer is assumed to have a strong dipole, where the siloxane surfaces have negative charges, while the aluminol surface exhibit positive charges. Consequently, the entity layers of kaolinite are strongly bonded by hydrogen and dipolar interactions. The boundaries of these layers enclose O atoms and OH groups [1]. Kaolin is a hydrated aluminum silicate. It has a wide variety of industrial applications, due to its sole physiochemical properties [2] Kaolin can be treated with mechanical, beneficiation, calcinations and chemical processes to prepare the material for use [3]. Kaolin originally exhibit white color with high kaolinite brightness, but it mainly contains various amounts

N. G. Habtu et al. (Eds.): ICAST 2019, LNICST 308, pp. 662–671, 2020.
https://doi.org/10.1007/978-3-030-43690-2_50

anatase (TiO_2), mica and iron oxides (Fe_2O_3), which provide low intensity and low quality [2]. The presence of such impurities is high-priced to the production of high-grade kaolin, so considerable reports have been dedicated to the problem of removing these contaminants with different treatment methods [4]. Separating the coarse particle like quartz and undesirable mineral such as mica is important steps. This is a simply process in case of a secondary deposit, but in contrast with the primary deposit as it is more difficult due to the presence of high proportion of the abrasive minerals that have survived the alteration process [5]. Industrial practice of kaolin minerals reveals physicochemical and mineralogical characteristics which make them very useful in many different applications [6, 7]. Typically, kaolin used in the paper industry where playing a dual role, as filler between the pulp fibers and as a surface coating for a white silky finish. To eliminate impurities, kaolin can be cleaned with a continuous high gradient magnetic separator to produce highly white material suitable for paper or porcelain [8]. The kaolin improvement is costly and in principle controlled by the composition. Therefore, the assortment different treatment techniques calcination temperature must be related to the physicochemical properties existing among the noticed mineral species [9, 10].

The major use of kaolin is in the paper industry (as filler and as a coating on the paper surface to enhance the printing) and the ceramics manufacture as additives [11]. Most of the industries required a great quality of the final products. Ethiopia imports kaolin abroad for industrial application even though the physicochemical and mineralogical properties of Ethiopian kaolin have been investigated which is good quality for industrial applications specifically which investigated for zeolite synthesis [12]. Ethiopian kaolin has impurity prior to iron oxides. This is the problem for not to use for different industrial application without treatment. So, the raw Ethiopian kaolin have undergone a certain treatment phase and was investigated the calcination temperature to obtain good quality metakaolin. As a result, the government should aware of Ethiopian kaolin can be used as industrial raw material with a basic treatment processes.

2 Methodology

2.1 Sample Collection

Kaolin used in this study was collected from south Gondar near debretabor city. Representative kaolin sample undergoes a mechanical size reduction, grinded and milled to passes less than 75 μm sieve. Size reduced kaolin was used for beneficiation, calcinations and characterization.

2.2 Beneficiation

To purify a certain impurities such as quartz, feldspar, mica, iron and titanium minerals and organic matter, wet processing is very important to produce industrial grade kaolin [13]. Mechanically treated kaolin was dispersed in water for stabilizing the kaolinite as a colloidal suspension and has been bunged so as to separate all agglomerate clay particles. The fine clay slurry has been dried at 60 °C for further analysis and characterization.

2.3 Calcinations

Wet treated kaolin was activated through calcination from 750 °C for 3 h to form reactive metakaolin. This is due to the calcinations temperature producing metkaolin is up to 850 °C as can be seen from the thermogravimetric analysis.

2.4 Characterizations of Kaolin

2.4.1 Thermal Analysis

TG-DSC curves of the air-dried sample were recorded using thermogravimeter (SDT Q600 V20.9 Build 20). Approximately 15.4 mg of sample was placed in a platinum crucible and was heated from ambient temperature, 20 °C, to 1000 °C. 100 mL/min supplied with nitrogen gas with a heating rate of 10 °C/min. Temperatures was calibrated by heating indium standards having a melting point of 156.6 °C at 10, 15 and 20 °C/min [14].

2.4.2 Mineralogy Study

Qualitative and quantitative characteristic of the phases, its crystallinity and the number of phases that is present in were determined by X-ray diffractometer MiniFlex 300/600 with Standard Sample Holder in a continuous scanning scan axis of 2theta/theta about a full scan of 36430 and scanning range from 10° to 70° anode material was used calcinations temperature having a K-Alpha1 wavelength and K-Alpha2 wavelength of 1.54059 and 1.54441 respectively.

2.4.3 Functional Group Determination with FTIR

Fourier Transformation Infrared, FTIR, spectrophotometer PerkinElmer (ILC38B6PD7) were used for qualitative characterization of surface functional groups of the kaolin. Infrared transparent pellets were made using KBr and transmittance was recorded within a scanning range of 400–4000 cm^{-1}.

2.5 Effect of Calcinations Temperature on Quality Metakaolin

pH value, surface area and brightness are the critical parameter which can affect the clay minerals (kaolin) to use for industrial application. This is dependent on the calcination's temperature. The effect of calcinations temperature on pH value and surface area were investigated.

2.5.1 pH Value

pH of the kaolin is important to use for industrial application. The pH solutions of raw and treated kaolin were measured as 1 g of kaolin powder in 100 ml of distilled water.

2.5.2 BET Surface Area Analysis

Surface area was measured with standard method by nitrogen adsorption and application of BET equation by means of Nova 4000e surface area and pore size analyzer. Measuring the number of N_2 molecules adsorbed at monolayer coverage, gives information needed for calculating the surface areas, which is calculated by the instrument. 0.5 g of the samples was weigh and loaded in to the BET glass sample tube, the weight of the tube before and after loading was recorded.

3 Results and Discussions

3.1 Thermogravimetry (TG-DSC) Analysis

Thermal analysis gives information on weight loss; crystallization/recrystallization, decomposition and phase transformation reveal the thermal behavior of the kaolinite structure [17]. The TG–DSC curves of the raw Ethiopian kaolin samples at 20–1000 °C are illustrated in Fig. 1. Up to 330 °C mass loss is ascribed both due to the surface moisture loss and the loss of the absorbed water molecules embedded in the kaolin and also the volatile organic matters that have been exhibited. Dehydroxylation continued up to 850 °C [18]. The DSC curve of kaolin showed a broad characteristic melting exothermic approximately 940 °C. This is due to the recrystallization and transformation of dehydrated substance to mullite, cristobalite, and quartz characteristic for metakaolin dissociation and formation of spinel [19].

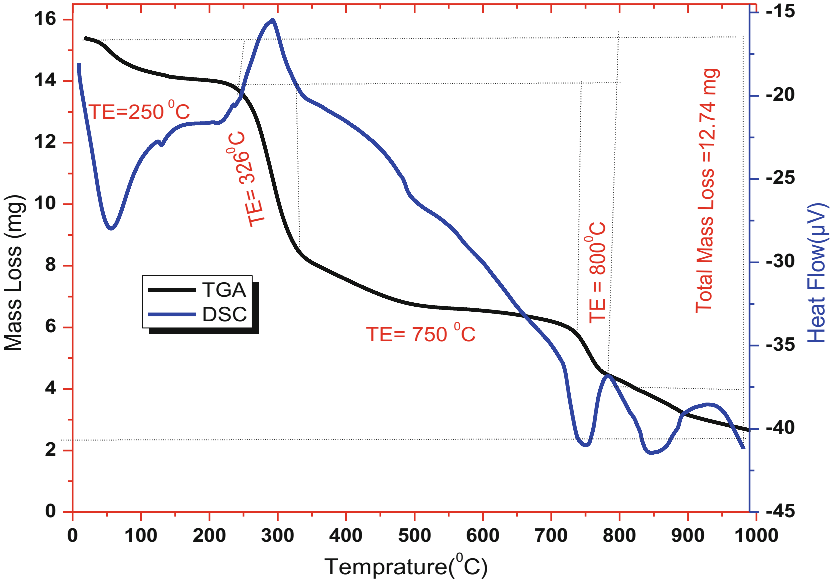

Fig. 1. TGA–DSC signals of kaolin.

3.2 Mineralogy with XRD

X-ray diffraction (XRD) result reveals structural defects in kaolin because of variability in the peak positions and modulation of their intensities in kaolin XRD patterns. XRD identification of order/disorder is challenging because of overlapping peaks and interferences in kaolin [20]. The degree of kaolinite XRD patterns exhibits sharp peaks between 2theta = 28 and 42 shown in Fig. 2 is a characteristic amorphous phase present metakaolin's [21]. The diffraction pattern shown in Fig. 2 is kaolin and quartz as the major minerals in metakaolin as well as raw kaolin. It was clear that the kaolin is mainly composed of kaolinite mineral as indicated from peaks existing from raw kaolin approximately at 2θ values are 28, 42 has been reported in previous studies [22]. This indicates that the kaolin used in this research is ideal kaolin with anorthic (triclinic) lattice structure. High proportion of quartz mineral was detected from peaks existing at 2θ values 28 metakaolin and small proportions 42 [23]. Figure 2 shows a small peak at 2θ = 20°, 24°, 35° and 42° from the calcined kaolin is an indication of deformed silica and alumina kaolinite materials [12]. As can be seen from the figure, calcined kaolin has shown low crystalline, amorphous, structure as compared with raw kaolin at the main kaolinite peaks 2θ = 28 and 42.

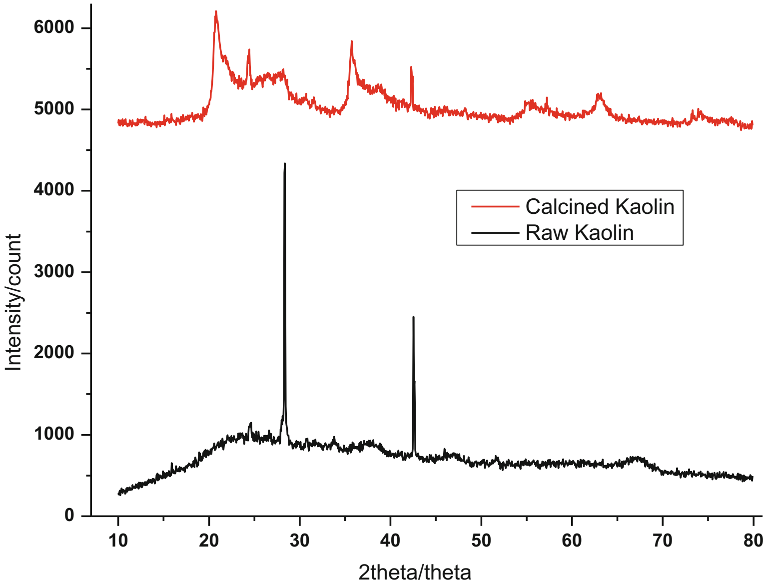

Fig. 2. X-ray diffraction patterns of calcined and raw kaolin

3.3 FTIR Analysis

FTIR spectral generally can be categorized into two regions as 4000–1300 cm^{-1} (functional group region) and 1300–400 cm^{-1} (finger-print region). The frequency assignment approach is adopted for the current investigation. As can be seen from the spectra Fig. 3, the bands placed between 3447 cm^{-1} regions corresponds to Si-OH stretching vibration both for raw and calcined kaolin and with the range of from 3625 to 3821 cm^{-1} small peak shows us to the inner layer OH (Al-O-H) stretching in the raw kaolin obtained by [20]. But no any peak at those of the calcined kaolin. From this it can be deduce that there is no hydroxyl group from the calcined kaolin. The absorption peak at 1114 cm^{-1} is assigned to Si-O in-plane stretching vibration. The bands placed at 1032 cm^{-1} region correspond to skeleton Si-O-Si in-plane stretching vibration. The FTIR spectra depict as predominance of kaolin mineral in the studied sample and did not show any peak for impurity such as smectite [24]. Si-O-Al bending vibration and Si-O bending vibration shows at 574 and 468 cm^{-1} respectively. The bending vibrations of water molecules adsorbed to kaolin surface (hygroscopic moisture) are responsible for the bands at 1635 cm^{-1} both in the raw and calcined kaolin. As can be seen from Fig. 3, the raw kaolin clearly shows sharp peak at those band but the calcined kaolin is insignificant exhibit due to the water molecule removed during thermal treatment. As can be seen, the percent transmittance of raw kaolin is much higher than the calcined kaolin. This is due to the decomposition of iron oxide during calcination responsible to the kaolin becomes red powder which will have less transparent than the raw (white powder) kaolin.

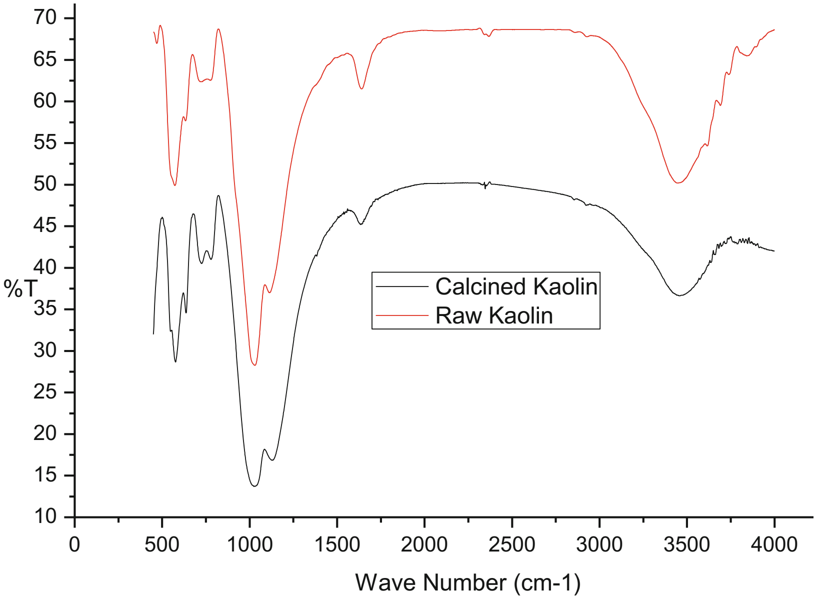

Fig. 3. FTIR- spectra of treated and raw kaolin (Color figure online)

3.4 Calcinations Temperature Effects on Active Kaolin

Surface Area (BET) Analysis

Figure 4 depicted as the surface area properties of raw, beneficiated, beneficiated with surfactant and reference kaolin with a thermal treatment from 550 °C and 1200 °C. Figure 4 shows as the calcination temperature increased there was a fast increase in the surface area up to 1050 °C, which can be accredited to the elimination of burnable impurities within the pores of the kaolin minerals, in the same way increase ease of access within the pores. From a calcination's temperature of 1050–1200 °C it can be seen that a dramatic decrease in the surface area of kaolin. This is the fact that as temperature increases the pore size increases with a subsequent Subside of the layer of the pores, leading to limited access within the material. That is the recrystallization which can formed structurally ordered spine kaolin.

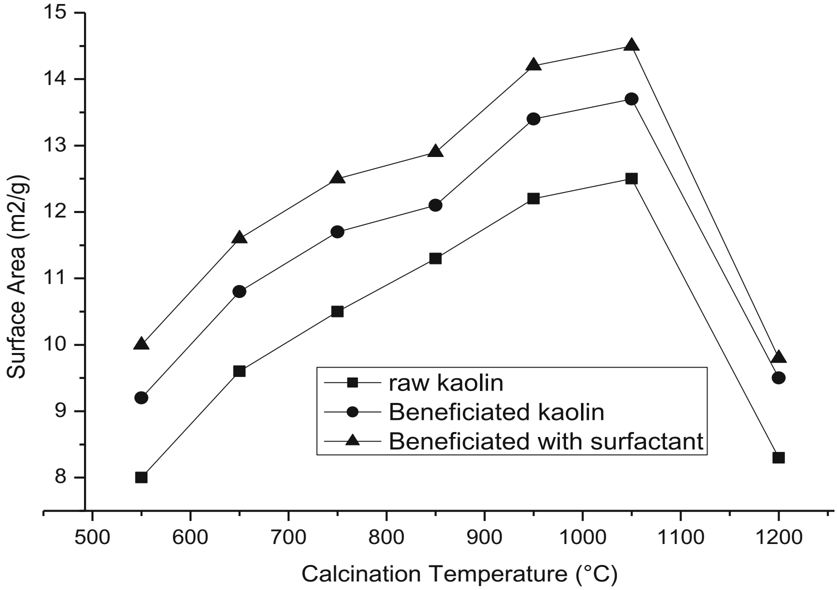

Fig. 4. Surface area of Raw, beneficiated and beneficiated with surfactant kaolin with calcination temperatures (550 °C–1200 °C)

Also, the surface area of beneficiated with surfactant treatment of Ethiopian kaolin is higher than the raw and beneficiated kaolin. This is due the surfactant can flock out the colloids materials as impurities. Even of beneficiated with surfactant and simple beneficiated kaolin have better surface area than the reference kaolin at 1050 °C which corresponds to the standard grade values for industrial application.

pH Value

Increasing the calcination temperature up to 750 °C, the pH values decrease and then increase to from 750–1200 °C as shown in Fig. 5. The decrease in pH in the metakaolin is possibly due to the kaolin rehydroxylation exploiting the OH functional groups shifted [25]. The pH values are different for the differently treated samples. As can be seen, the pH value of raw kaolin is acidic at the calcination temperature of 750 °C. But the pH value comes to neutral as go far to the calcination's temperature 850 °C and above. This is the fact that dissociated iron impurities at the most reactive (amorphous) kaolin having acidic medium. The pH value neutral far to the high calcination's temperature is due to iron recrystallizations to for spinel and mulite formations. Beneficiated with surfactant sample shows better (neutral) pH value than others even the reference kaolin initially and calcinations above 850 °C. As a result, beneficiation weather in simple or with chemical modifications is better treatment techniques for their neutral pH range values of kaolin.

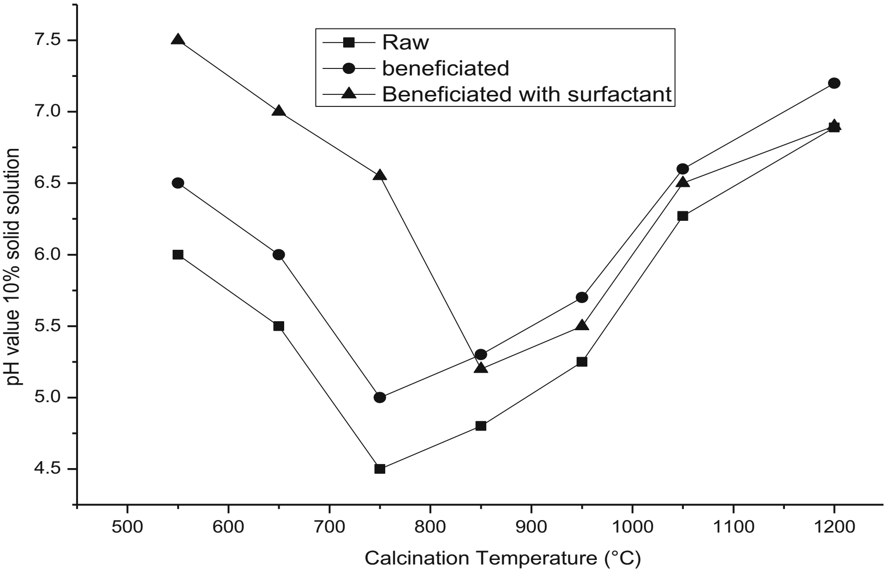

Fig. 5. Change in pH with calcination temperature

4 Conclusion

Quality of the kaolin was investigated with different treatment techniques. The calcination temperature has an effect on the surface characteristics and pH values the kaolin. Chemical modification can improve the surface area and pH values of the raw kaolin with indicate that the good grade industrial raw materials. From the thermal analysis, the calcinations temperature can be enough from 550 °C–900 °C for their good surface properties. The low weight loss up to 300 °C conforms as insignificant moisture and volatile organic matter which is suitable for industrial application. Impurities in raw kaolin are more as compared to treated kaolin which impacts the physicochemical properties. However, the treatment processes reduce the iron percentage to a lower level. From the FTIR and XRD spectra analysis, the main component exhibits the kaolinite material.

References

1. Chun-Hui, Z., John, K.: Clays and clay minerals: geology, properties and uses. Appl. Clay Sci. **74**, 58–65 (2013)
2. Asmatulu, R.: Removal of the discoloring contaminants of East Georgia kaolin clay and its dewatering. Turkish J. Eng. Environ. Sci. **26**, 447–453 (2002)
3. Mukherjee, S.: The Science of Clays: Applications in Industry, Engineering and Environment. Springer, Dordrecht (2013). https://doi.org/10.1007/978-94-007-6683-9
4. Du, F., Li, J., Li, X., Zhang, Z.: Improvement of iron removal from silica sand using ultrasound-assisted oxalic acid. Ultrason. Sonochem. **18**, 389–393 (2011)
5. Prasad, M.S., Reid, K.J., Murray, H.H.: Kaolin: processing, properties and applications. Appl. Clay Sci. **6**, 87–119 (1991)
6. Murray, H.H.: Applied Clay Mineralogy, 1st edn. Elsevier, Amsterdam (2007)
7. Chatterjee, K.K.: Uses of Industrial Minerals, Rocks and Freshwater. Nova Science Publishers Inc., New York (2009)
8. Yavuza, C.T., Prakash, A.B., Mayoa, J.T., Colvina, V.L.: Magnetic separations: from steel plants to biotechnology. Chem. Eng. Sci. **64**, 2510–2521 (2009)
9. Kogel, J.E., Trivedi, N.C., Barker, J.M.: Industrial Minerals and Rocks: Commodities, Markets and Uses, 7th edition. Society for Mining, Metallurgy, and Exploration, Inc., Littleton (2006)
10. Chandrasekhar, S., Ramaswamy, S.: Influence of mineral impurities on the properties of kaolin and its thermally treated products. Appl. Clay Mineral. Sci. **21**, 133–142 (2002)
11. Murray, H.H.: Major kaolin processing developments. Int. J. Miner. Process. **7**, 263–274 (1980)
12. Aragaw, T.A., Ayalew, A.A.: Removal of water hardness using zeolite synthesized from Ethiopian kaolin by hydrothermal method. Water Pract. Technol. **14**, 145–159 (2018)
13. Aroke, U.O., El-Nafaty, U.A., Osha, O.A.: Properties and characterization of kaolin clay from Alkaleri, NorthEastern Nigeria. Int. J. Emerg. Technol. Adv. Eng. **3**, 387–392 (2013)
14. Archer, J.D., Douglas, W.M., Brad, S.: The effects of instrument parameters and sample properties on thermal decomposition: interpreting thermal analysis data from Mars. Planet. Sci. **2**, 1–21 (2013). https://doi.org/10.1186/2191-2521-2-2
15. Twyman, R.M.: Wet Digestion. Elsevier Ltd., London (2005)
16. Potts, P.S.: A Handbook of Silicate Rock Analysis, pp. 47–58. Blackie and Sons Ltd., Glasgow (1992)
17. Hongfei, C., Qinfu, L., Jing, Y., Songjiang, M., Ray, L.F.: The thermal behavior of kaolinite intercalation complexes-a review. Thermochim. Acta **545**, 1–13 (2012)
18. Hongyan, W., Chunshan, L., Zhijian, P., Suojiang, Z.: Characterization and thermal behavior of kaolin. J. Therm. Anal. Calorim. **105**, 157–160 (2011). https://doi.org/10.1007/s10973-011-1385-0
19. Aragaw, T.A., Kuraz, F.: Physico-chemical characterizations of ethiopian kaolin for industrial applications: case study WDP propoxur formulations. In: Zimale, F.A., Enku Nigussie, T., Fanta, S.W. (eds.) ICAST 2018. LNICST, vol. 274, pp. 122–134. Springer, Cham (2019). https://doi.org/10.1007/978-3-030-15357-1_10

20. Peter, A.A., Yahaya, M.S., Wan, M.A.W.D.: Kaolinite properties and advances for solid acid and basic catalyst synthesis. RSC Adv. **5**, 101127–101147 (2015)
21. Kenne, D.B.B., Elimbi, A., Cyr, M., Dika, M.J., Tchakoute, H.K.: Effect of the rate of calcinations of kaolin on the properties of metakaolin-based geopolymers. J. Asian Ceram. Soc. **3**, 130–138 (2015)
22. Goulash, M., Buhl, J.-Ch.: Geochemical and mineralogical characterization of the Jabal Al-Harad Jordan for its possible utilization. Clay Miner. Mineral. Soc. **45**, 281–294 (2010)
23. Bundy, W.M., Murray, H.H.: The effect of aluminum on the surface properties of kaolinite. Clays Clay Miner. **21**, 295–302 (1973). https://doi.org/10.1346/CCMN.1973.0210505
24. https://www.indiamart.com/proddetail/olinpowder7107133755.html. Accessed June 2018
25. Burhan, D., Emin, C.: Investigation of central anatolian clays by FTIR spectroscopy. Int. J. Nat. Eng. Sci. **3**, 154–161 (2009)
26. Velho, J.A.L., Gomes, C.S.F.: Influence of calcination on physical and technological properties of kaolin’s for paper filler applications. Geol. Carpath. Clays **45**, 21–26 (1994)