

Treatment of a Nigerian Kaolin ore for Improved Industrial Application

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Abstract

A study was carried out on leaching of Nigerian kaolin ore by Oxalic acid ($C_2H_2O_4 \cdot 2H_2O$). The raw kaolin ore from Share, North central Nigeria was characterised by EDXRF (X-ray fluorescence) and major constituents were SiO_2 , Al_2O_3 , and minor amounts of K_2O , Na_2O , CaO , TiO_2 , along with colour-imparting Fe_2O_3 and MnO that need to be removed to upgrade the kaolin suitability for industrial usages. The effects of parameters such as $C_2H_2O_4$ concentration, temperature, and particle size were investigated. Under the standard leaching conditions of $-75+63 \mu m$ particle size, $75^\circ C$ and $0.15 \text{ mol/L } C_2H_2O_4$, about 78.5% of kaolin ore was reacted within 120 minutes. Comparison of the EDX analysis of the raw and leached kaolin showed removal efficiency of 97.1% for the iron at optimal leaching conditions. Energy of activation of 17.65 kJ/mol was obtained in the study supports the proposed diffusion control mechanism for the dissolution process.

Keyword: Kaolin, Oxalic acid, Leaching, dissolution kinetics, Iron removal.

1. Introduction

Kaolin is dominantly composed of kaolinite ($Al_2Si_2O_5(OH)_2$), which is a hydrous clay mineral, and an important member of the kaolinite group [1]. Kaolin has a wide and diverse range of industrial applications, as raw material in paper coating, plastic, ceramics, cosmetics, paints, porcelain, potteries, pharmaceutical and brick manufacturing [2, 3]. Kaolinite has a simple structure consisting of one tetrahedral silica sheet linked through oxygen to an octahedral alumina layer. Similarly, this mineral is also commonly used in waste

treatment and production of many industrial goods such as fertilizers, white colouring pigments and filler materials. The quality and commercial value of kaolin largely depend on its percentage purity, texture, whiteness and brightness colour properties [4-10]. The main impurities that are present in kaolin and often affect its industrial utilizations are iron oxides. Some researchers have developed different physical, chemical even recently microbiological method of treating kaolin with the aim of removing or reducing the iron contents present [11-20]. Oxalic acid is known for its ability to leach iron oxide and also has lower risk of contaminating the treated material after processing because of its high acid strength, reducing power and good complexing properties when compared to other organic acids [10]. Therefore, the aim of this work was to primarily investigate the performance of oxalic acid in the treatment of Nigerian kaolin sourced from the north central zone for improved industrial applications. Vast deposit of kaolin ore is predominant in the studied area and relevant data in this area of research is not available.

2. Materials and methods

2.1 Materials

The kaolin ore used for this study was obtained from Geological Survey Unit of the Kwara State Ministry of Solid Minerals, Ilorin, Nigeria. The kaolin ore was sourced from Share, Irepodun Local Government Area of Kwara State, Nigeria.

2.2 Leaching Procedures

The leaching tests were carried out in a 250 ml glass reactor which was kept stirred with a magnetic stirrer hot plate. For each run, 100ml of oxalic acid solution ($C_2H_2O_4$ reagent grade) at different concentration (0.01-0.2mol/L) were added to the flask and temperatures were set to the desired value. A 10.0g/L of kaolin was added to the reactor while under moderate stirring periodically (5-120 minutes). Experiments were done in duplicate, analyses and results averaged. However, the results are not different by not more than 5%. The variables studied were the concentration of oxalic acid (0.1-1.5), temperature (25°C-75°C) and particle size (-75+63, -112+90 and -250+112 μ m) [13, 21]. Appropriate kinetic plots were done to determine the order of reaction and activation energy for better understanding of the dissolution mechanism for the process. Residual product at optimal leaching was characterized by XRD and SEM techniques.

3. Results and Discussion

3.1 Characterization Studies

The result of elemental analysis of Share Kaolin sample by Energy Dispersive X-ray Fluorescence (EDXRF) gave SiO_2 (58.60 %), Al_2O_3 (29.5%), TiO_2 (2.71%), Fe_2O_3 (2.34%), MgO (0.53%), Na_2O (0.26%), K_2O (1.52%) and MnO (0.021%).

The mineralogical purity by XRD (Fig. 1) shows the dominance of kaolinite ($Al_2Si_2O_5(OH)_4$) {06-221} and trace amounts of Illite ($(K,H_3O)Al_2(Si_3Al)O_{10}(OH)_2 \cdot xH_2O$) {24-0141} and quartz (SiO_2) {083-0539}. The structural morphology of the raw kaolin sample by SEM micrography (Fig. 2), gave fragments with crystal pores. The pores were fine along with coarse surface crystal formation, expected of a named kaolin ore.

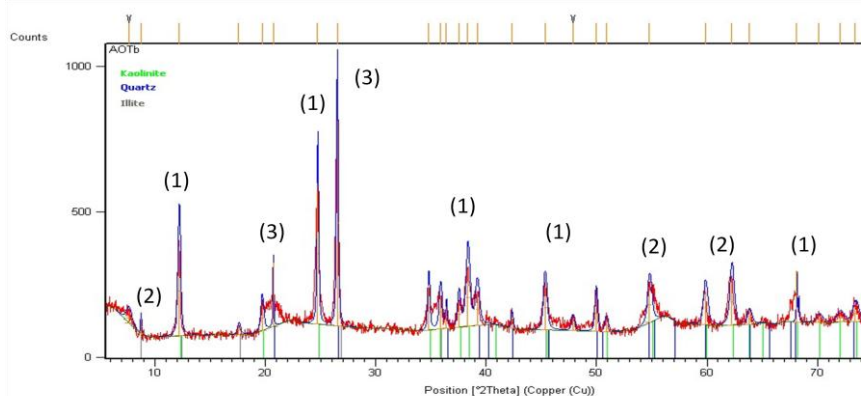


Figure 1. XRD pattern of raw kaolin ore showing important compounds detected with joint committee on powder diffraction file numbers responsible for the peak attribution: (1) Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) {06-221}, (2) Illite ($(\text{K},\text{H}_3\text{O})\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$) {24-0141} and (3) quartz. (SiO_2) {083-0539}.

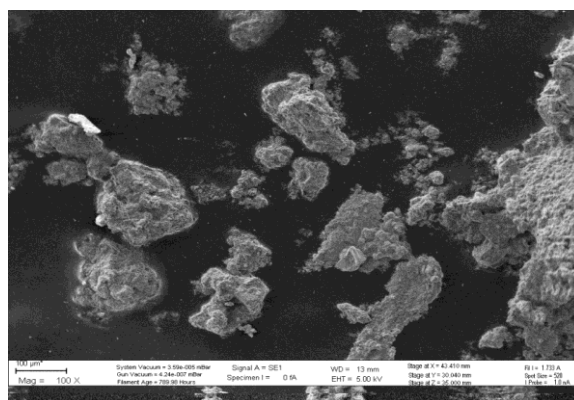


Figure 2. The SEM micrograph of the raw kaolin ore

3.2 Leaching studies

3.2.1 Effect of Oxalic acid concentration

The effect of Oxalic acid concentration on the dissolution of kaolin ore dissolved has been examined as a function of constant time at various Oxalic acid concentrations and are summarized in Fig. 3.

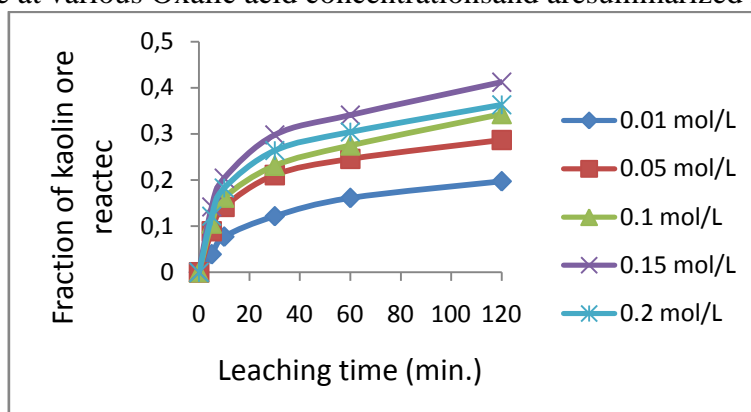


Figure 3. Variation in oxalic acid concentrations with time for kaolin ore dissolution at 55 °C

Experimental conditions: Temperature = 55°C, Oxalic acid Concentration = 0.01-0.20 mol/L, w/v = 10g/L with moderate stirring.

From Fig. 3, it is observed that an increase in oxalic acid concentration leads to an increase in the dissolution of kaolin. For example, dissolution reached 41.2% at 0.15 mol/L and decreases moderately at 0.2 mol/L when 36.3% dissolution was obtained. The reason for the drastic reduction in amount of kaolin reacted may be due to the possible precipitation phenomenon [24, 25].

3.2.2 Effect of Temperature

The experiments to determine the effect of temperature on 10g/L kaolin ore dissolution by 0.15 mol/L oxalic acid solution were carried out with temperature ranging from 25 – 75°C. The result of this investigation is shown in Fig.4. It is evident from Fig.4 that the extent of ore dissolution increases with increasing temperature. The dissolution rate increases linearly as the reaction temperature increases. This means that the dissolution of kaolin ore is also dependent on reaction temperature. However, it was recorded that at 75°C, 78.5% of the kaolin ore reacted within 120 minutes. However, temperature beyond 75 °C was not considered in this study as there may exist excessive loss of acid through evaporation at higher temperature [21]. Also, about 22% of the unleached residue was analysed to contain silica (SiO_2 : 083-0539) [24] and this could serve as raw materials for some defined industries.

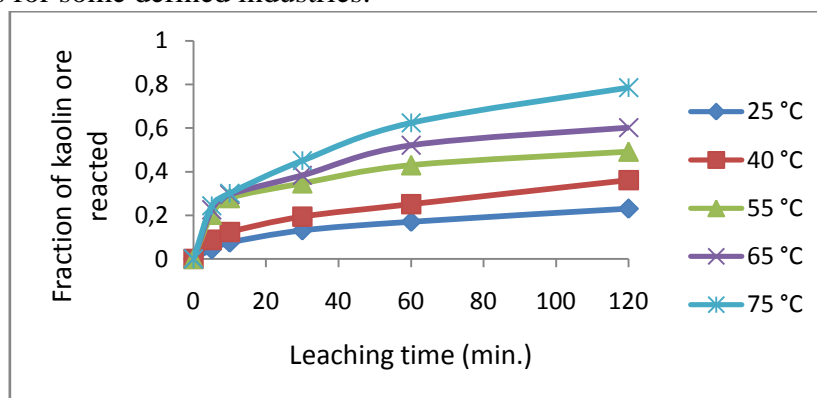


Figure4. Variation in reaction temperature with time for kaolin ore dissolution at temperature 25-75 °C.

3.2.3 Effect of particle size

The effect of particle size on the extent of kaolin ore dissolution was experimented using three different particle size fractions: -75+63, -112+90 and -250+112 μm . The dissolution rate increases with decreasing particle size as shown in Fig. 5. At a set of experimental/or optimal conditions, 48.1%, 63.4% and 78.5% reacted within 120 minutes using -75+63, -112+90 and -250+112 μm , respectively.

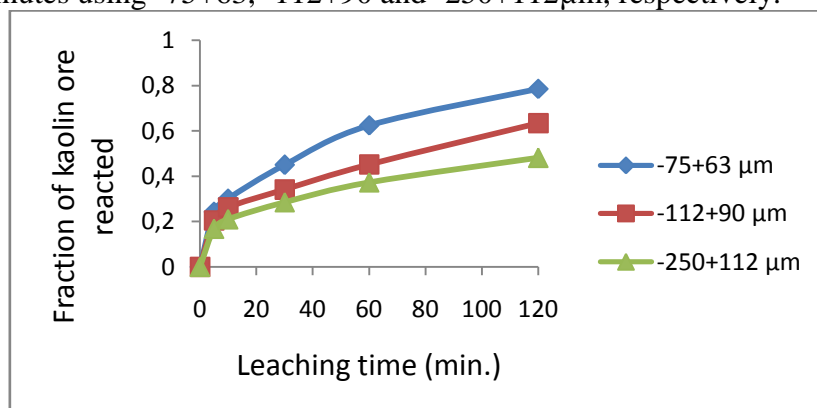


Figure5. Effect of particle size on the kaolin ore dissolution in 0.15 mol/L $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ at 75 °C
Experimental conditions: Temperature = 75 °C, Solid to liquid ratio 1g/100ml (w/v) = 10g/L, $[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}] = 0.15 \text{ mol/L}$.

3.3 Discussion

3.3.1 Dissolution kinetics analysis

In general, fluid-solid reactions have many importance. For example, in the ore leaching process, the change in solid particle size can be neglected during the heterogeneous reaction, if the ore contains large amount of unreacted impurities in presence of non-flaking ash. Thus, in this kind of reaction rate, there are some physical steps that can affect the extent of dissolution, in addition to the chemical reaction, such as diffusion through the fluid film and/ or inert solid layer of the reactant or product. By using Shrinking Core Model (SCM), it is thought that the dissolution reaction takes place on the outer surface of the solid as the reaction proceeds, leaving behind an inner solid layer called “ash layer” and the unreacted shrinking core [22-26]. Therefore, the dissolution data obtained in this study were evaluated using two shrinking core models:

The chemical model:

$$1 - (1 - \alpha)^{1/3} = \frac{k_c M_k C_A t}{\rho_b a r_0} = k_r t \quad (1);$$

The diffusion model:

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = \frac{k_c M_k C_A t}{\rho_b a r_0} = k_d t \quad (2)$$

In equations (1) and (2),

k_c is the first-order rate constant (min^{-1}), M_k is the molecular weight of the kaolin reactant (kgmol^{-1}), C_A is the acid concentration (molm^{-3}), D is the diffusion coefficient ($\text{m}^2\text{min}^{-1}$), d is the density of the particle (kgm^{-3}), r is the initial radius of the particle (m), α is the fraction of kaolin ore dissolved at time t (min), μ is the stoichiometric coefficient, $k_1(\text{min}^{-1})$ and $k_2(\text{m}^2\text{min}^{-1})$ are the overall rate constants. It is important to note that, of the two shrinking core models tested, only equation (2) was found to give a perfect straight line, with a good correlation R^2 of 0.973 as compared to the R^2 value of 0.593 exhibited by equation (1) data fittings. Consequently, the dissolution data in Fig.3 (effect of the leachant concentration), Fig. 4 (effect of reaction temperature) were accordingly treated using SCM equation (2) to obtain the following plots:

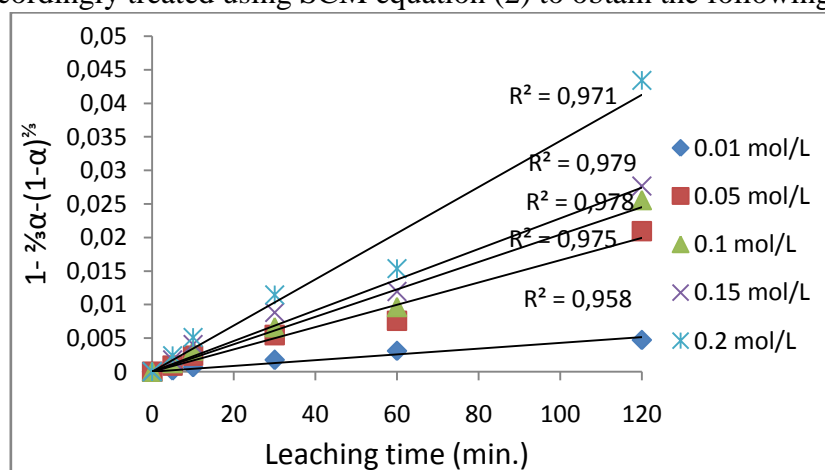


Figure 6. Plot of $1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$ versus leaching time at different $(\text{COOH})_2.2\text{H}_2\text{O}$ concentrations using the diffusion controlled model.

The experimental rate constants, k_1 , were evaluated from the slopes in Fig.6 and the plot of $\ln k_1$ vs $\ln[(\text{COOH})_2.2\text{H}_2\text{O}]$ were made as illustrated in Fig.7.

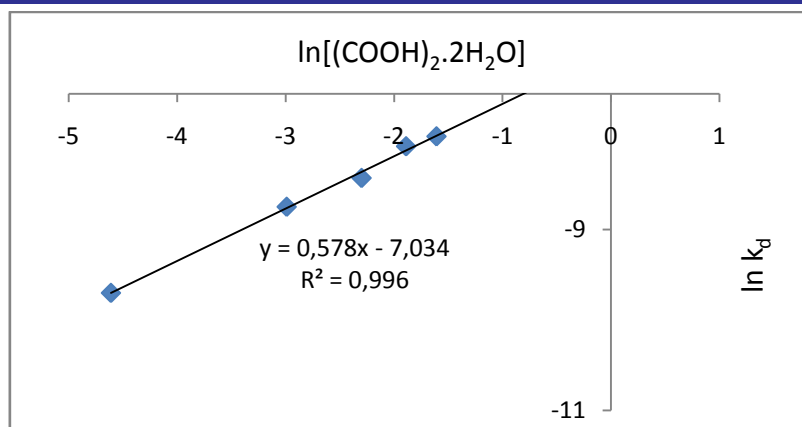


Figure 7. Plot of $\ln k_d$ versus $\ln[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}]$

The slope of the resulting plot (Fig. 7) gave the dissolution reaction order of $0.9965 \approx 1.0$, with respect to hydrogen ion concentration, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ for concentrations ≤ 0.15 mol/L. This shows that the dissolution reaction follows a first order mechanism. Furthermore, the linearization of the data in Fig. 4 (effect of reaction temperature) was done using equation (2) as illustrated in Fig. 8.

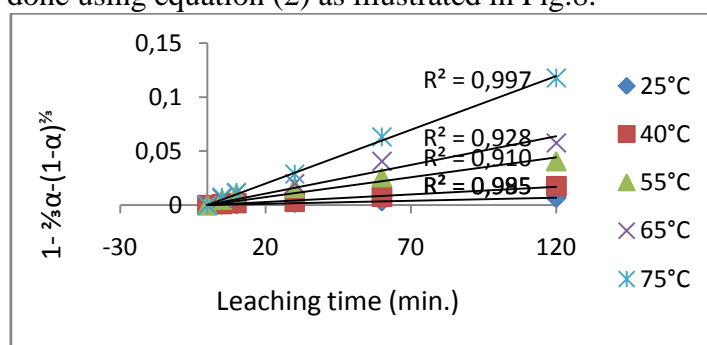


Figure 8. Plot of $1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$ versus leaching time at different temperatures.

The rate constant for variation of temperatures (25 – 75 °C), to obtain energy of activation E_a , can be accomplished by the following Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (3)$$

Therefore, the plot of $\ln k$ versus $1/T$ data for temperature range (25 – 75 °C) is summarised in Fig. 9.

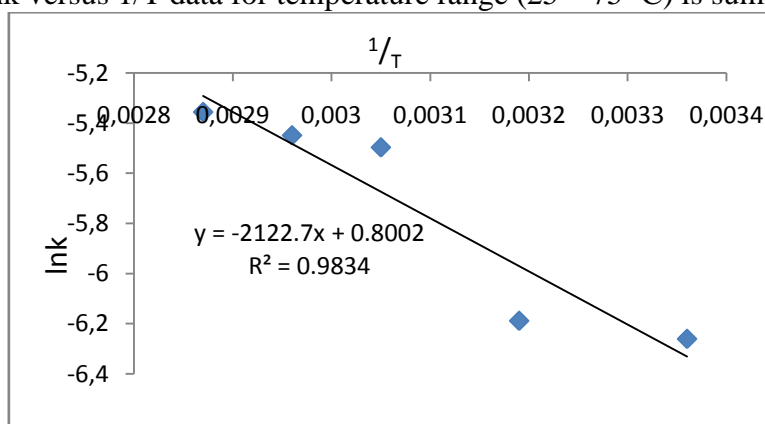


Figure 9. Arrhenius relation of reaction rate against the reciprocal of temperature, the data extracted from Fig. 8.

From Fig. 9, the activation energy was estimated to be 17.65kJmol^{-1} , supporting the fact that dissolution kinetics of the investigated kaolin ore was by diffusion controlled process.

In order to evaluate the rate determining step for the dissolution process by $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ solution, the linearization of the kinetic data from Fig. 5 was carried out using the diffusion control core model (equation 2) as illustrated in Fig.10.

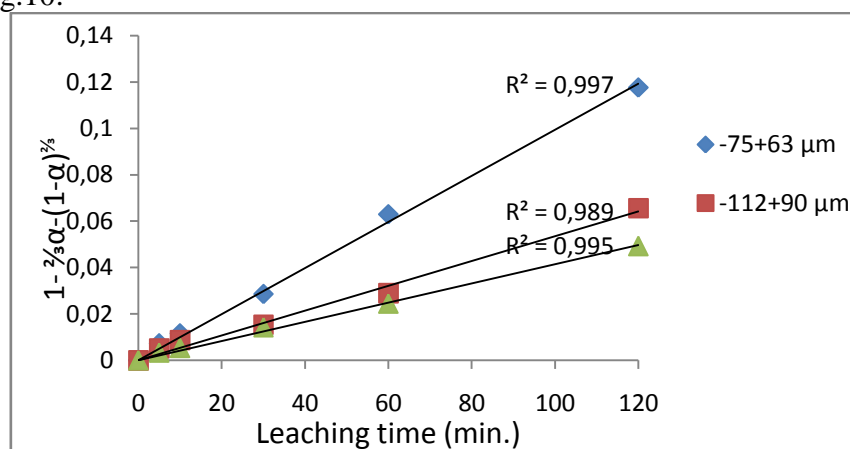


Figure 10. Plot of $1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$ versus leaching time for different particle size.

To further support the proposed mechanism, the value of the rate constant k_d were then plotted against the reciprocal of the particle radii $(1/r_o)^2$ yielding a linear relationship with a correlation coefficient of 0.9914.

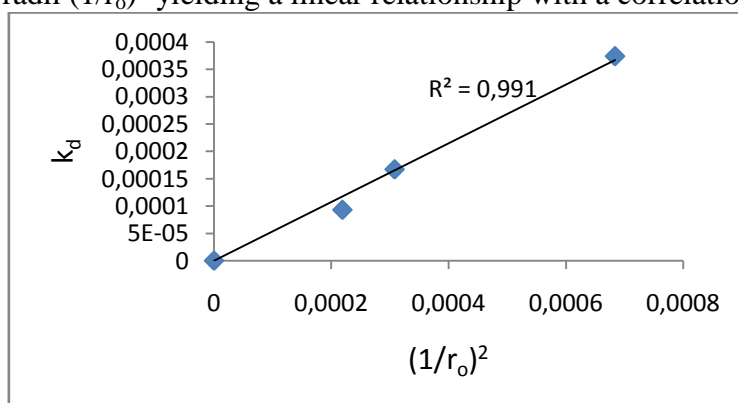


Figure11. Plot of k versus $(1/r_o)^2$

The linear dependence of the rate constant on the square of inverse of the particle size radius showed that the rate controlling step for the dissolution of the kaolin ore occur via diffusion control mechanism as illustrated in Fig.11. However, the plot of k_d against $(1/r_o)$ did not give a perfect straight line [24].

3.3.2 Residual Product Analysis

The result of the residual product by XRD analysis (Fig. 12) showed that the processed kaolin after optimal leaching interpreted by the Joint Committee on Powder Diffraction Standard File number (JCPDS) numbers showed that it contains pure Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) free of iron and α -quartz, (SiO_2). Also, the SEM micrograph of the residual product at optimal leaching (0.15mol/L, 75°C) 120 minutes, of the unreacted kaolin, particles exhibit erosive and fragmented particles during treatment by 0.15 mol/L oxalic acid at 75°C

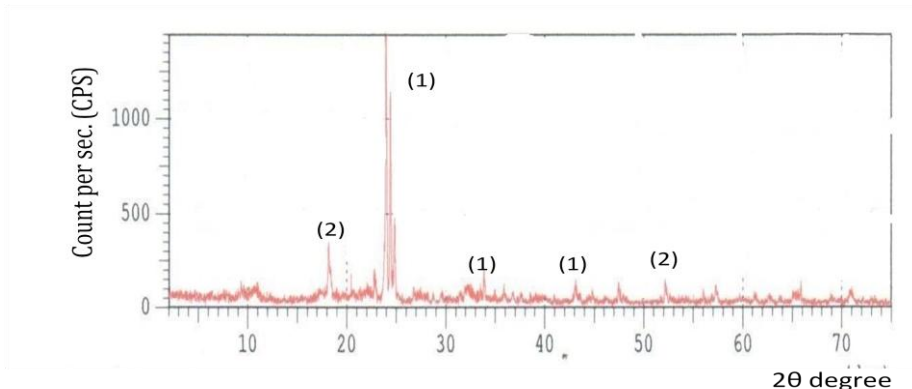


Figure 12. XRD spectra of the residual product at optimal leaching: (1) Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) {06-221}; (2) α -quartz, (SiO_2) {083-0539}.

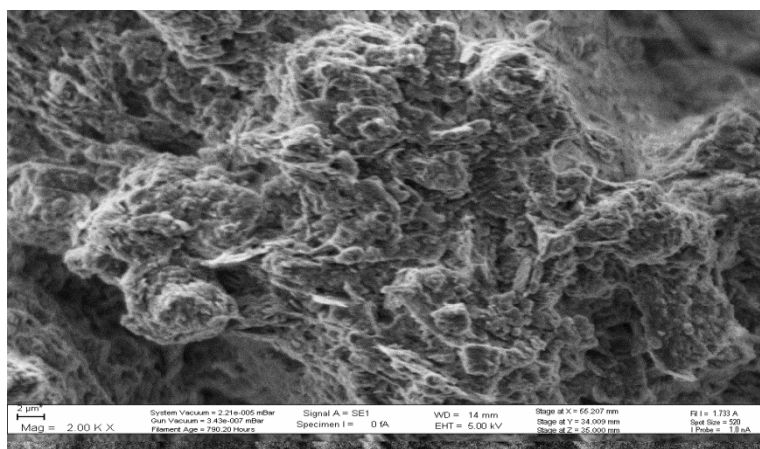


Figure 13. SEM image of the unreacted kaolin particle at optimal leaching

However, to ascertain the improved product for industrial utilization, the products obtained at optimal leaching was subjected to EDX analysis as depicted thus (Fig. 14a and b).

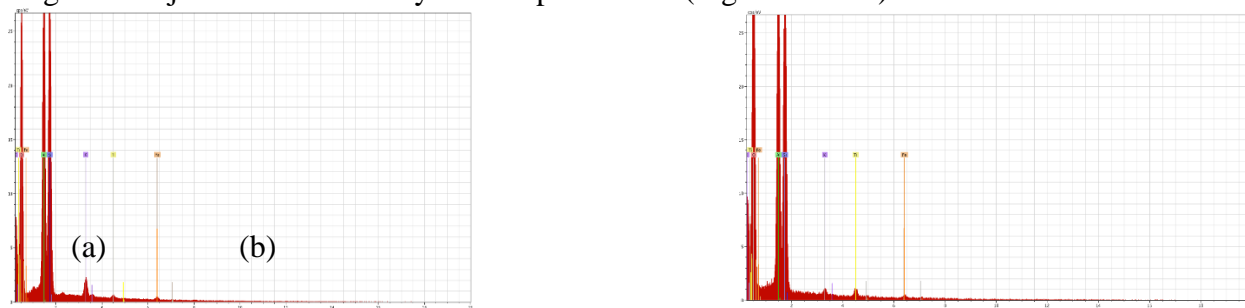


Figure 14. (a) Raw kaolin before leaching; (b) Processed kaolin after leaching

Also, the major mineral elements detected by the EDX equipment is summarised in Table 1.

Table 1. Major elements in the raw (before leaching) and processed kaolin (after optimal leaching)

Element	Oxygen	Aluminium	Silicon	Potassium	iron	Titanium
Before leaching (%)	62.00	18.59	17.15	1.56	1.04	0.62
After leaching (%)	64.30	16.28	17.03	1.04	0.03	0.29

From table 1, it is evident that there is loss of elements such as Silicon, Aluminium, Potassium and especially iron after optimal leaching during treatment with 0.15 mol/L oxalic acid solution at 75 °C for 120 minutes. It is important to note that assessment of kaolin ore for a named industrial value depends primarily

on the extent of iron removal. Hence, in this study drastic decrease of iron component from initial 1.04% to 0.03% yielding 97.1% efficiency.

4 Conclusion

In this study, the oxalic acid leachant was used in the treatment of a Nigerian kaolin ore for improved industrial applications. During the process, increased acid concentration, reaction temperature and decreasing particle size of the pulverized ore greatly increases the extent of the ore dissolution. At optimal condition of (0.15mol/L oxalic acid solution, temperature 75 °C), the dissolution reached 78.5% with 120 minutes using -75+63µm sized particle. The unleached residue ($\approx 22\%$) was analyzed contain silica, a valuable by-product for some industries. The dissolution data were analyzed and was found to fit diffusion control model. The dissolution reaction is a first order relation and the calculated activation energy of 17.65 kJmol^{-1} supported the proposed mechanism. Finally, the extent of iron removal by EDX analysis (a measure of improved industrial value) at optimal leaching gave 97.1%.

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