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REMOVAL OF IRON IMPURITIES FROM A NIGERIAN BIOTITE-RICH KAOLINITE ORE BY A SULPHURIC ACID SOLUTION

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ABSTRACT

The significant rise in demanding for pure aluminum and aluminum compounds of an industrial value addition from kaolinite ore cannot be over emphasized. Thus, with a wide array of industrial applications in paper filling, refractories, porcelain, adsorbent, catalysis, rubber and paint additives, possible improvement of whiteness and brightness properties of a Nigerian Biotite-rich Kaolinite ore is investigated in sulphuric acid media. During the leaching investigations, parameters such as the reaction temperature, the leachant concentration and the particle size affecting the extent of the ore dissolution are accordingly examined. 85.1 % of the initial 10 g/L ore reacts within 120 min under the optimal leaching conditions (2.5 mol/L H_2SO_4, 75°C). The dissolution curves obtained in correspondence with the shrinking core model are analyzed and found to conform to the proposed surface diffusion reaction, as the activation energy is calculated to be 24.9 kJ/mol. The unreacted product (~24.9 %) analyzed by XRD is found to contain siliceous impurities ($MnSiO_3$: 45-209-1788) which could serve as a viable material for some defined industries.

Keywords: biotite, kaolinite, sulphuric acid, leaching.

INTRODUCTION

Due to the significant rise of the industrialization and the manufacturing processes, the demand for pure aluminum and aluminum compounds of industrial utilities cannot be over emphasized. Kaolinite, $Al_2Si_2O_5(OH)_4$, of a molecular weight of 258.07 g/mol, is made up of aluminosilicate layers of octahedral AlO_2OH_4 and tetrahedral SiO_4 sheets of 1:1 alternative arrangement [1 - 3]. It is inexpensive, easily accessible and whitish of a chemical composition referring to 46.54 % SiO_2, 39.50 % Al_2O_3 and 13.96 % H_2O [4 - 6]. It has promising characteristics of a porous material which make it an excellent contaminants adsorbent [7]. Kaolinite is usually formed by the alteration of K-feldspar either by weathering or hydrothermal processes. Kaolin and its varieties are versatile materials that find a wide array of utilizations as ceramics, paper, paints, fiberglass, inks, pharmaceuticals, plastics and porcelain production [8 - 11]. Thus, the presence of associated impurities particularly iron and titanium which are responsible for the brownish-yellow coloration of kaolin greatly alter its quality (i.e. its whiteness and brightness properties) and significantly limits its commercial viability [12, 13]. The pertinent stage of the manufacturing of an industrially viable crude material refers to the efficient and effective removal of iron oxide matrixes from kaolin bearing ores. The iron and other impurities removal from kaolinite ore is therefore of a paramount importance. It is usually carried out via techniques such as froth flotation, magnetic separation, gravity separation, jigging, reductive roasting, biological leaching and acid treatment [14 - 16].

Acidic media have been majorly applied to the purification and upgrading of kaolin ore for industrial value additions due to their efficiency and the lack of generation of a significant environmental menace [2, 17 - 19]. This chemical treatment technique involves leaching of the kaolinite mineral with organic acids (oxalic, citric and ascorbic acid) and inorganic acids (hydrofluoric, hydrochloric, sulfuric and perchloric acid), thereby causing a disaggregation of the kaolinite ore, an elimination of the associated gangues and a dissolution of the outer layers [20, 21]. However, due to the fact that iron and other matrixes associated with kaolin may be either tightly bonded or occur in a complex form, the aforementioned methods (magnetic separation, froth flotation etc) often have poor impurities extraction efficiencies [22].

Sulphuric acid is chosen to be used as a lixiviant in the leaching investigations and the possible elimination of associated gangues (Fe, Ti, Mn etc) contained in biotite-rich kaolinite ore of Nigerian origin. This is determined by its bleaching power, high selectivity and chemical stability [23]. The investigation is carried out aiming to tackle effectively and efficiently the shortcomings pointed above.

EXPERIMENTAL

Materials

The kaolinite ore used for this investigation was sourced from Nane Didan Bungudu Local Government Area of Zamfara State, Nigeria. The clay was crushed, grinded and sieved by the American Standard Test Method (ASTM) to four particle sizes: −75+45 μm, −90+63 μm, −112+90 μm and −134+107 μm, respectively. The finest particle size of −75+45 μm, assumed to have a larger surface area, unless otherwise stated, was used for all experiments in this study. All reagent used were of analytical (BDH) grades, while deionized water was used for the preparation of all aqueous solutions.

Methods

Leaching investigations

The leaching study was performed in a Pyrex leaching reactor of 600 mL capacity at moderate stirring and refluxing, coupled with a thermometer and a thermostat. A 10 g/L of the pulverized ore was added to the agitated solution at defined lixiviant concentration at a specified reaction temperature, varied time intervals (5 min -120 min) and various sulphuric acid concentrations (0.1 mol/L - 2.5 mol/L). The extent of the kaolinite ore dissolution varied over the time. After the completion of the leaching tests, the leached solution was filtered, water-washed, oven-dried and re-weighed. The concentration which gave the highest fraction dissolved was used for the subsequent optimization of the other parameters such as the reaction temperature and the particle size variations. Also, from the relevant Arrhenius relations, the activation energy, Ea, and the Arrhenius constants were obtained. However, the residual products obtained at optimal leaching conditions were analyzed by XRD, EDS and SEM analyses for material purity tests [21, 24, 25].

RESULTS AND DISCUSSION

Ore characterizations

The elemental composition of kaolinite ore examined by EDXRF MINIPAL model refers to: SiO_2 (23.98 %), Fe_2O_3 (8.59 %), Al_2O_3 (3.76 %), K_2O (2.59 %) and MnO_2 (0.03 %), respectively [26]. As examined by EDS, the parent ore contains oxygen (42.34 %), aluminum (2.62 %), silicon (13.44 %), iron (1.97 %), and carbon (38.61 %) [26]. The XRD (model Empyrean PANALYTICAL) results verify that kaolinite ($Al_{2\cdot00}Si_{2.00}O_{9.00}$: 96-900-9231), biotite ($Mg_{6.55}Fe_{3.46}Al_{5.29}Ti_{1.34}Si_{11.36}K_{4.00}O_{48.00}$: 96-900-0844) and quartz ($Si_{3.00}O_{6.00}$: 96-900-9667) are the major compounds present in the ore [26]. The photomicrograph analysis summarized in Fig. 1 is also in a good conformity with the findings that the ore is majorly consisted of biotite, kaolinite and quartz minerals.

As shown in Fig. 1, biotite has a brownish pleochroic with characteristic perfect cleavage; *quartz* has a low

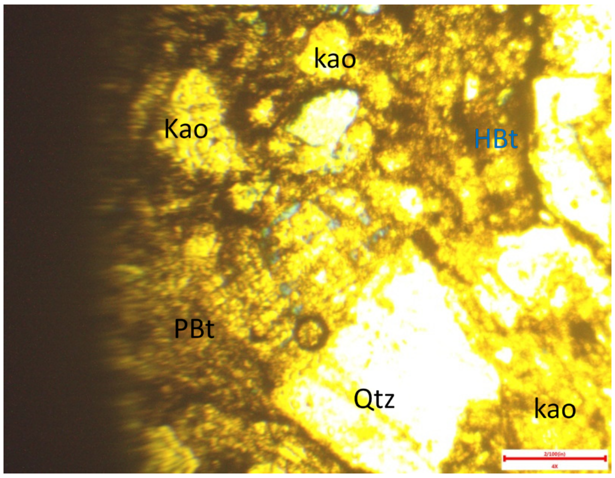

Fig. 1. Photomicrograph analyses of raw biotite-rich kaolinite ore (kao = kaolinite, Qtz = Quartz, PBt = Primary biotite, HBt = Hydrothermal biotite).

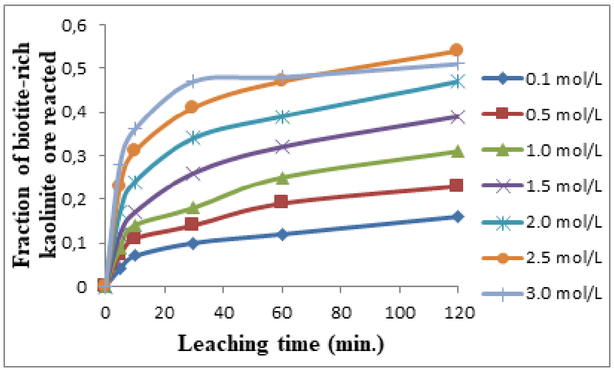

Fig. 2. A fraction of biotite-rich kaolinite ore reacting at different concentrations of sulphuric acid. (H_2SO_4 = 0.1 mol/L - 2.5 mol/L, a reaction temperature of 55°C, a particle size of -75+45 μm).

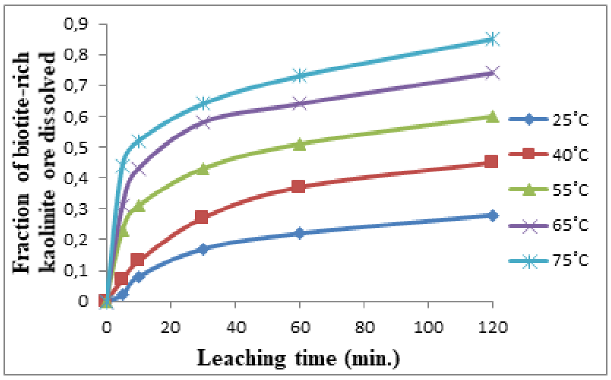

Fig. 3. An effect of the reaction temperature on the fraction of the ore dissolved. (H_2SO_4 = 2.5 mol/L, a reaction temperature of 25°C - 75°C, particle size of -75+45 μm).

relief, a shining appearance and undulatory extinction; kaolinite is characterized by pseudo-hexagonal habit like many other clay minerals [27].

Leaching studies

An effect of the acid concentration

The effect of sulphuric acid (H_2SO_4) concentration on the extent of kaolinite ore dissolution is studied within the acid range of 0.1 mol/L - 2.5 mol/L at 55°C. The amount of the ore reacting in presence of different sulphuric acid concentrations at different leaching times is shown in Fig. 2.

As summarized in Fig. 2, the fraction of the ore treated increases faster with an increase of the sulphuric acid concentration from 0.1 mol/L to 2.5 mol/L. The extent of the ore dissolution reaches values of 16.4 % and 54.2 % within 120 min at a leaching temperature of 55°C at a sulphuric acid concentration of 0.1 mol/L and 2.5 mol/L, respectively. The extent of the ore reacted decreases from 54.2 % to 51.3 % with a further increase of the leachant concentration from 2.5 mol/L to 3.0 mol/L at the conditions pointed out.

However, the curve appreciably flattens in presence of 3.0 mol/L sulphuric acid. This could be attributed to precipitation formation and kaolin structure collapsing at higher acid concentration [28, 29]. As reported in the literature [30], the chemical reaction between kaolinite and sulphuric acid is described by the following stoichiometric equation:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2SiO_2 + 5H_2O \qquad (1)$$

An effect of the reaction temperature

Experiments are carried out with −75+45 μm particle fraction in the temperature range of 25 °C - 75°C in 2.5 mol/L sulphuric acid solution at moderate stirring aiming to study the effect of the reaction temperature on the ore dissolution extent. The corresponding plots are shown in Fig. 3.

Fig. 3 indicates that the dissolution rate is highly sensitive in respect to the reaction temperature. The extent of the fraction reacted increases appreciably within 120 min from 28.2 % to 85.1 % with the temperature increase from 25°C to 75°, respectively. This result conforms with those of other studies [31], where the extent of the ore dissolution is found significantly increasing with the reaction temperature increase. The availability of a kinetic energy responsible for molecules collusion during the ore leaching [32] can be a possible reason for the increased dissolution observed. However, temperatures beyond 75°C are not considered because of a loss of the solution through evaporation.

An effect of the particle size

The effect of the ore particle size on the extent of ore dissolution is studied by varying the size fraction. The latter refers to -75+45 μm, −90+63 μm, and −112+90 μm, while the other parameters are kept constant (a reaction temperature of 75°C and a sulphuric acid concentration of 2.5 mol/L). The results obtained are summarized in Fig. 4.

Fig. 4 shows that the rate of dissolution increases with the decrease of the ore particle size at optimal con-

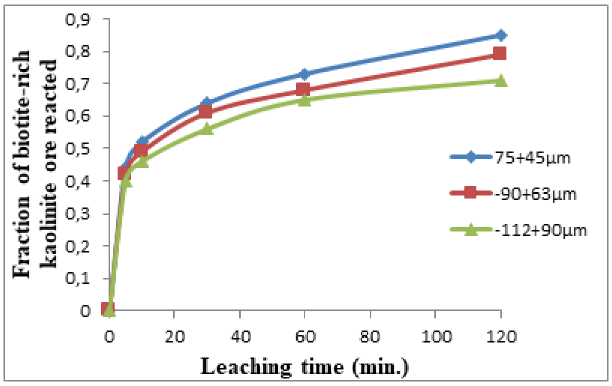

Fig. 4. A fraction of the treated kaolinite ore versus the leaching time in case of a different particle size.

ditions. The fraction of the kaolinite ore treated within 120 min at 75°C in 2.5 mol/L H_2SO_4 solution refers to 85.1 %, 79.0 % and 71.3 % in case of a particle size of−75+45 µm, −90+63 µm and −112+90 µm, respectively. This could be attributed to the fact that the finest particles provide a larger surface area for a contact with the free hydrogen ions [24]. It is worth adding that there are metal ions present in the leachate of the following amounts: 1729.1 mg/L of Al^{3+}, 1.59 mg/L of Fe^{3+}, 48.2 mg/L of Ca^{2+}. There are also traces of other metal ions. The purification of the pregnant solution for a possible beneficiation will be reported in due course.

Discussion

A kinetic analysis

Attempts are made to fit all experimental data (runs at different reaction temperatures and leachant concentrations) into a shrinking core model mechanism (SCM). The latter is applied to describe the leaching kinetics. The simplified equations of the model are presented in refs. [33, 34]. If the reaction rate is controlled by a chemical interaction in the inert product layer, the integrated rate equation is consistent with Eq. (2):

$$[1-(1-x)^{1/3}]=Kt \qquad (2)$$

However, if the reaction is controlled by a diffusion step, Eq. (3) is obeyed:

$$[1-\frac{2}{3x}-(1-x)^{2/3}]=Kt \qquad (3)$$

where x is the fraction reacted, t is the reaction time, while

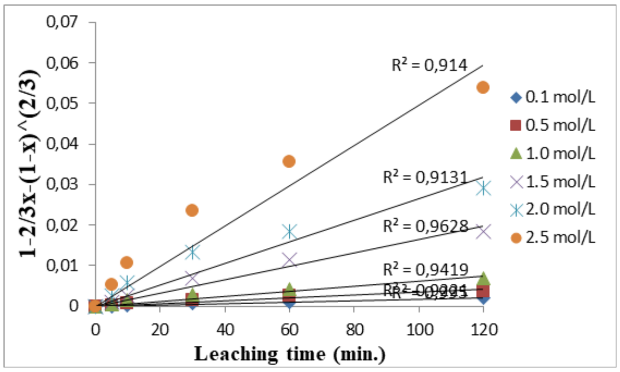

Fig. 5. Plots of $1-\frac{2}{3x}-(1-X)^{2/3}$ versus the leaching time as a function of the acid concentration used. (The conditions are identical with those of Fig. 2).

K is the reaction rate constant obtained by Eqs. (2) and (3). The dissolution data in Figs. 2 - 4 is appropriately fitted into Eqs. (2) and (3) of SCM. It is important to note that it perfectly fits Eq. (3) with an average correlation (R^2) value of 0.995 as compared to the R^2 value of 0.532 obtained in case of Eq. (2). Therefore, the dissolution process by a sulphuric acid lixiviant is apparently dominated by a diffusion-controlled mechanism described by Eq. (3). The dissolution data in Fig. 2 is linearized with the application of Eq. (3) aiming to estimate the reaction order. The results obtained are shown in Fig. 5.

The of K obtained with the application of Eq. (3) are used to present the Arrhenius plot, lnK versus ln[H_2SO_4]. The derived slope of 0.8403 from Fig. 6, with a correlation coefficient of 0.943, reveals a first order dissolution relationship in case of the leachant concentrations used.

The dissolution data of Fig. 3 is linearized with the application of Eq. (3) to obtain the plot in Fig. 7:

Fig. 7 provides the presentation of appropriate plots of

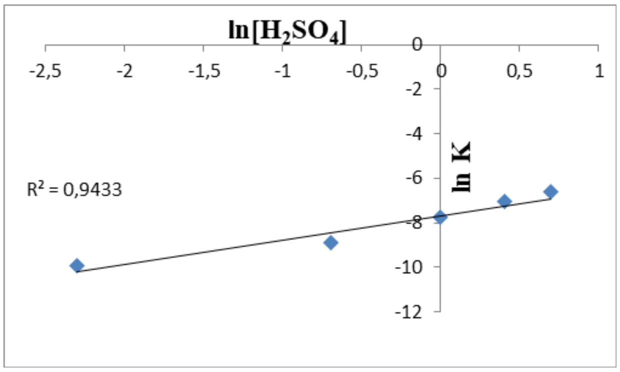

Fig. 6. Plot of lnK against ln [H_2SO_4]. (The conditions are identical with those of Fig. 4.)

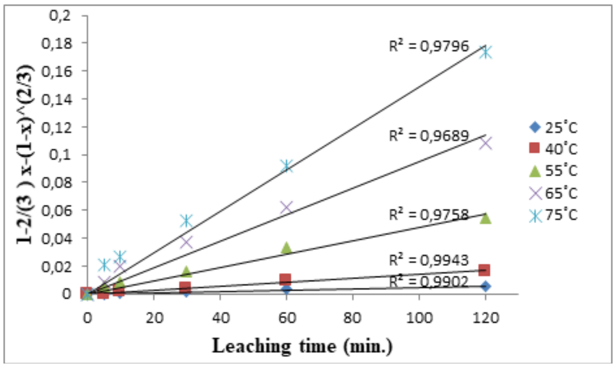

Fig. 7. A plot of $1 - \frac{2}{3x} - (1 - X)^{2/3}$ versus the leaching time at different reaction temperatures. (The conditions are identical with those of Fig. 3).

lnK versus 1/T(K^{-1}) which in turn lead to determination of the apparent activation energy by the Arrhenius equation:

$$K = Aexp(-Ea/RT) \qquad (4)$$

where K is the reaction rate constant (min^{-1}), A is the frequency factor (min^{-1}), Ea is the activation energy (kJ/mol), R the universal gas constant (8.314 J/K mol), while T is the absolute temperature (K).

The activation energy, Ea, of the dissolution of kaolinite ore found on the ground of Fig. 8 amounts to 24.9 kJ/mol. This value is in correspondence with the proposed diffusion mechanism. It is also in-line with the value reported in ref. [35] which is found equal to ~20 kJ/mol. From an economical perspective, the result of this study is far better when compared to the value of 97 kJ/mol found in ref. [36]. It is worth adding that according to the literature, an activation energy higher than 40 kJ/mol implies that the mechanism is controlled by a chemical reaction, while an activation energy lower than 40 kJ/mol suggests a diffusion reaction as a rate controlling step [36, 39, 27].

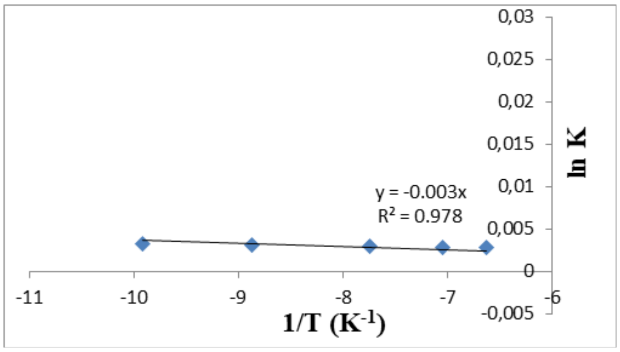

Fig. 8. An Arrhenius relation of lnK versus 1/T(K^{-1}).

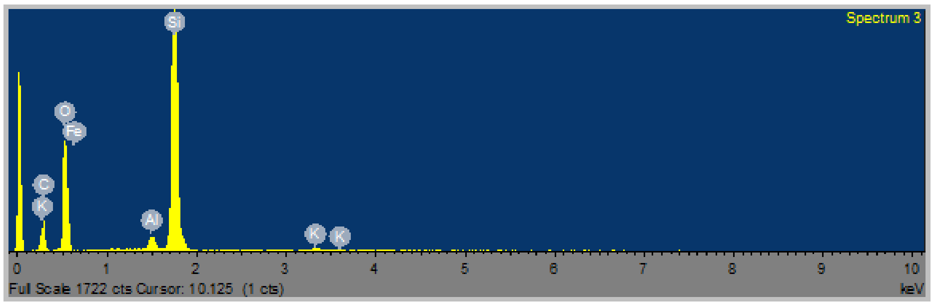

Fig. 9. An EDS spectrum of the H_2SO_4-leached residue of the kaolinite ore under optimal conditions.

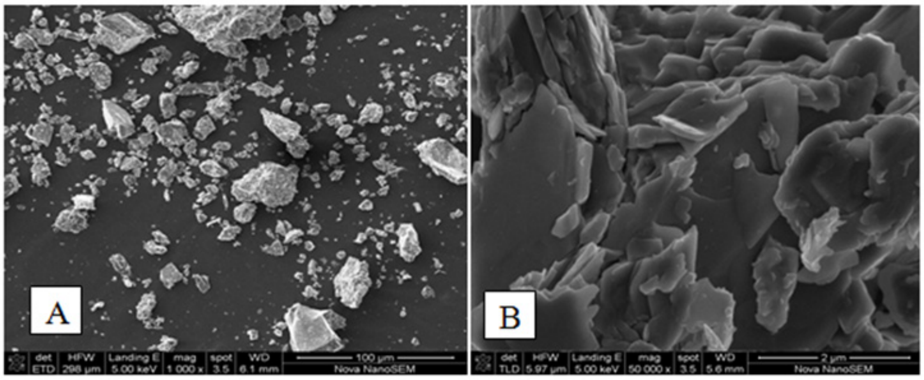

Fig. 10. SEM micrographs of the H_2SO_4-leached residue of kaolinite ore under optimal conditions.

Residual product analyses

The elemental composition of the residual product obtained under optimal conditions is examined by EDS. The results obtained are shown in Fig. 9. They show the presence of Al (5.56 %), Si (17.02 %), O (47.9 %) and C (26.3 %), which in turn is in correspondence with the data obtained by XRD referring to siliceous impurities ($MnSiO_3$: 45-209-1788). The results obtained show that the residual product could serve as a viable material for some defined indigenous industries. The SEM pattern of the acid-leached residue at optimal leaching conditions (75°C, 2.5 mol/L H_2SO_4, a size of −75+45 μm) shown in Fig. 10(A) reveals that the un-reacted product has a typical sheet shape containing embedded particles characterized by irregular bulk edges and surfaces [37, 38]. However, the flake-like amorphous temporary phase generated is inescapable as verified by the aluminosilicate formation in Fig. 10 (B) [38 - 40].

CONCLUSIONS

The present investigation is focused on the examination of the extent of kaolinite ore dissolution by H_2SO_4 as a lixiviant. An optimization of some parameters such as the reaction temperature, the lixiviant concentration and the particle size in respect to the extent of the ore dissolution is carried out. The results obtained suggest that the dissolution rate increases significantly with the increase of the lixiviant concentration and the reaction temperature and decreases appreciably with the increase of the particle size. 85.1% of the initial 10 g/L ore reacts within 120 min at optimal leaching conditions (75 °C, 2.5 mol/L H_2SO_4, a size of −75+45 μm), while the un-reacted product contains siliceous impurities according to the XRD and EDS examinations. It could serve as a viable material for some defined industries. The apparent activation energy of the process is found equal to 24.9 kJ/mol, which indicates a diffusion-controlled mechanism of the process. The results of this study show that sulphuric acid is attractive, efficient and effective for leaching a kaolinite ore of Nigerian origin aiming industrial utilizations.

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