Comparative Study of Chemical And Biological Methods of Beneficiation of Kankara Kaolin

Ajayi, O. A & S. S. Adefila

ABSTRACT:- Kaolin is a clay mineral that has a wide application in the industry, depending on its purity. The quality of kaolin mined around the world is depleting especially with depth and rate of mining. Consequently, the usability of this mineral is threatened by the presence of some inherent impurities. Beneficiation enhances kaolin applications; hence, it becomes imperative to understudy comparative means of upgrading kaolin, for the process integration and optimization. In this work, chemical and biological leaching of iron rich kaolin sample was carried out using sulphuric acid, oxalic acid, cultured and un-cultured *Aspergillus niger* (*A. niger*). The kinetics of leaching determined from XRF analysis was observed to be higher for acid compared to biological method and at shorter contact time. The conversion of alumina for oxalic, sulphuric, un-cultured and cultured *A. niger* were determined to be 77.81, 87.73, 26.38 and 28.37, respectively; while that of iron were 66.07, 98.32, 25.71 and 28.51. The kaolin leached with un-cultured *A.niger* was observed to digest both alumina and iron at an enhanced rate in the first 6 days, while the cultured remained inactive due to adaptation, for the same number of days. The cultured *A.niger* was later observed to leach more than the un-cultured one despite the adaptation period, it went through.

Keywords:- bioleaching, Kankara kaolin, *Aspergillus niger*, iron removal, dealumination, acidolysis,

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1.0 INTRODUCTION

Kaolinite clay with formula $Si_2Al_2O_5(OH)_4$, is the major mineral component of kaolin, which may usually contain quartz and mica and also, less frequently, feldspar, illite, montmorillonite, ilmenite, anatase, heamatite, bauxite, zircon, rutile, kyanite, silimanite, graphite, attapulgite, and halloysite [1],[2],[3]. Kaolin essentially finds applications in porcelain, nuclear waste treatment, pottery, paper, pigment, and filler manufacturing [4],[5],[6] as well as for cracking catalysts and adsorbent production [7],[8],[9]. The extent of their applications depends greatly on associated unique physical, physicochemical and chemical properties, which gladly could be tailored by means of various approaches. Established approaches involve chemical, mechanical and physical methods are froth floatation, gravity and magnetic separation, reductive roasting, size reduction by hydro cyclone, selective flocculation and acid treatment/leaching [10],[11],[12],[13]. The preferred beneficiation methods of kaolin minerals depend on the amount and nature of the mineral impurities associated to it. Although these methods are quite useful in removing impurities, they are, at the same time, costly, complicated and environmentally hazardous. Bioleaching processes are usually more economical, ecofriendly, and uses less amount of energy compared to other methods [14],[15],[16]. *A. niger* is one of the most widely used fungi in bioleaching, which is used commercially in the production of organic acids, such as citric acid [17], oxalic acid [18], and gluconic acid [19]. These acids have found application as lixivants for the leaching of heavy metals from ore materials, kaolin and solid wastes [13],[16],[20],[21], and may reduce the environmental impacts resulting from the inherent impurities or mode of treatment [22].

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A. niger has also been found to overproduce organic acids that can serve as leaching agents for the solubilisation of Al, Fe, Mn, Ni, Pb, Cd,Cu, Zn from fly ash [23] and leaching of heavy metals in contaminated soil [24]. Accordingly, various authors have employed this microorganism for the purpose of beneficiating kaolin material [4],[12], while others used combinations of enzymes for the same goal [13], [16],[25]. Nigeria has huge reserve of kaolin, which spreads all over the country, but continuous and progressive study on this mineral deposit, points to increased level of impurities, with depth of mining resulting to limited application. In order to improve the quality of kaolin for enhanced usage, the colouring agents and/or inherent impurities must be removed or reduced through more economic and ecofriendly techniques. Accordingly, this paper understudy a comparative approach (biological and chemical) for beneficiating kaolin sourced from Kankara village, Katsina State, Nigeria.

2.0 MATERIALS AND METHODS

2.1 Chemicals and Starting Materials

All the reagents used in this study were of analytical standard. Clay of kaolinite origin was mined from Kankara village of Katsina State, Nigeria, and used appropriately in this work. It is termed red raw Kankara kaolin (RRK) due to its reddish appearance. The *A.niger* strain used in this work was cultured from isolated pistachio shell, obtained from the Department of Microbiology, Ahmadu Bello University, Zaria. Nigeria.

2.2 Clay Beneficiation and Activation

The removal of some impurities from raw clay was first done by physical separation of dirt, followed by the wet/soaking process, following the step reported by Ajayi et al [26]. The beneficiated kaolin (BRK), which still retained its red colour was then air and oven dried at 125^0C for 24hrs, prior to crushing using jaw crushers (model PE 150*250 SBM), ball milled and sieved. The beneficiated kaolin was activated through thermal treatment in a muffled furnace at 800^0C for 6hrs, resulting to formation of metakaolin (BMK). The metakaolin was subsequently employed for both acid leaching and biological treatments.

2.3 Isolation of *A. niger* from Pistachio Shell and Culture Media

The fungus strain was isolated from pistachio shell agar (PDA) on potato dextrose agar and czapak dox agar (CZ) following Streak method. Fungi growth observed was later confirmed to be *A. niger*, following the identification method established by Klich [27]. The *A. niger* was collected raw, dried, crushed and kept under vacuum for further use.

2.4 Leaching of Metakaolin

The thermally treated kaolin, termed metakaolin, was subjected to leaching using acid and *A. niger*. The *A. niger* employed in this work was divided into two parts: namely cultured (described in Section 2.4.4) and un- cultured *A. niger*, while acid leaching was done using sulphuric and oxalic acid.

2.4.1 Acid leaching using sulfuric acid

The approach method for thermal heating during dealumination by Ajayi et al [26] was adopted. The content was then filtered, repeatedly washed with distilled water to remove any unspent acid, dried in oven, calcined at 400^0C for 2hrs and ground in a mortar pestle to powder form. The sulfuric acid treated samples are referred to as SK5, SK10, SK15, SK20, SK25 and SK30, where the numbers refer to different reaction time.

2.4.2 Acid leaching using oxalic acid

About 50g of metakaolin was mixed with various concentrations of oxalic acids (80%, 70%, 60%, 50% and 40%) in 500ml two-neck round bottom flash. The flask was equipped with a reflux condenser, placed on thermo regulated heating mantle, with temperature set at 105^0C. The reaction time was set at 30minutes initially to ascertain the optimal acid concentration, using ferric ion removal as litmus test. The content was repeatedly washed with distilled water to remove any unspent acid, filtered, dried in oven, calcined at 400^0C for 2hrs and ground in a mortar pestle to powder form. After this, oxalic acid strength of 60% was chosen for further investigation, while the reaction time was varied between 5 and 30mins, in interval of 5mins. The resulting slurry was quenched, repeatedly washed with distilled water, filtered, dried in oven, calcined at 400^0C for 2hrs and ground in a mortar pestle to powder form. The oxalic acid treated samples are referred to as OK5, OK10, OK15, OK20, OK25 and OK30, where the numbers refer to different reaction time.

2.4.3 Bioleaching using un-cultured A. niger

About 3g of *A. niger* was diluted with 94 ml distilled water and stirred till homogeneity. To this, about 20g of beneficiated kaolin was added and allowed to settle. The resulting content was placed in 500ml Erlenmeyer flasks in the absence of culture medium, sealed with removable cotton and incubated statically under anaerobic conditions at 30^0C, shaken intermittently at 160rpm, but period of incubation was varied from 0 to 10 days, in the interval of 2days. On completion of the specified period of incubation, the samples were washed thoroughly with water, dried and ground in a mortar pestle to powder form. The un-cultured *A. niger* treated samples are referred to as UAN2, UAN4, UAN6, UAN8 and UAN10, where the numbers refer to different reaction time.

2.4.4 Bioleaching using cultured A. niger

The same procedure described in Section 2.2.3 was repeated, except that the fungus was grown in culture medium consisting of (g/ltrs): starch, 1; $MgSO_4.7H_2O$, 0.1; $CaCO_3.7H_2O$, 0.1; KH_2PO_4, 0.1; $FeSO_4.7H_2O$, 0.01; ominimycin antibiotics, 0.1. The volume was made up to 500ml with distilled water, prior to introduction of beneficiated kaolin into the flask, with the culture media inoculated at a concentration of 10^6spores/ml. All experiments were performed in duplicate, and the average of the results reported, were with 4% deviation. The cultured *A. niger* treated samples are referred to as CAN2, CAN4, CAN6, CAN8 and CAN10, where the numbers refer to different reaction time.

3.0 RESULTS AND DISCUTIONS

3.1 Kaolin Pre-treatment and Production of *A. niger*

The chemical analysis for the raw kaolin revealed that the sample is very rich in ferric iron as depicted in Table 1. The high ferric iron content which imparts red colouration to the raw kaolin (RRK) renders this raw clay unfit for aesthetically related uses. The raw, beneficiated and calcined kaolin, respectively, have the following formulae:

$$2.38SiO_2 \bullet Al_2O_3 \bullet 0.37Fe_2O_3 \bullet 0.09MgO \bullet 0.02CaO \bullet 0.006Na_2O \bullet 0.01K_2O \quad raw$$
$$2.02SiO_2 \bullet Al_2O_3 \bullet 0.38Fe_2O_3 \bullet 0.08MgO \bullet 0.02CaO \bullet 0.003Na_2O \bullet 0.01K_2O \quad beneficiated$$
$$1.92SiO_2 \bullet Al_2O_3 \bullet 0.34Fe_2O_3 \bullet 0.08MgO \bullet 0.02CaO \bullet 0.004Na_2O \bullet 0.01K_2O \quad calcined$$

It is evident from these empirical formulae that the silica-alumina ratio, which is 2:1 for pure kaolinite, improves from raw to beneficiated kaolin - an indication of the extent of beneficiation. The silica content for the calcined sample was observed to reduce below theoretical, indicating desilicalization of kaolin at elevated temperature. Concurrently, the *A. niger* produced was found to conform comfortably with Klich method of identification. It was also decided that freshly extracted *A. niger* be used, in order to avoid extra cost of sub-culturing and purification.

Table 1: Compositional analysis for samples treated at various conditions

Sample ID	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
BRK	0.6313	0.3120	0.1170	0.0255	0.0061	0.0010	0.0039
RRK	0.6985	0.2930	0.1073	0.0270	0.0052	0.0016	0.0030
BMK	0.6328	0.3300	0.1118	0.0278	0.0059	0.0015	0.0037
OK5	1.0642	0.1668	0.0459	0.0228	0.0039	0.0013	0.0034
OK10	1.2517	0.1329	0.0444	0.0273	0.0039	0.0011	0.0032
OK15	1.3183	0.1112	0.0429	0.0298	0.0041	0.0013	0.0030
OK20	1.3467	0.0965	0.0398	0.0305	0.0038	0.0015	0.0027
OK25	1.3735	0.0732	0.0379	0.0258	0.0038	0.0010	0.0029
SK5	1.1737	0.1235	0.0287	0.0213	0.0039	0.0023	0.0024
SK10	1.2050	0.1066	0.0164	0.0213	0.0027	0.0018	0.0021
SK15	1.1737	0.0817	0.0054	0.0220	0.0025	0.0013	0.0016
SK20	1.1737	0.0714	0.0024	0.0208	0.0036	0.0021	0.0014
SK25	1.1737	0.0405	0.0019	0.0225	0.0034	0.0023	0.0010
CAN2	0.6708	0.3265	0.1113	0.0038	0.0057	0.0024	0.0035
CAN4	0.6847	0.3343	0.1114	0.0035	0.0057	0.0015	0.0037
CAN6	0.6793	0.2863	0.1115	0.0030	0.0055	0.0021	0.0039
CAN8	0.7653	0.2519	0.1038	0.0030	0.0063	0.0015	0.0038
CAN10	0.7872	0.2429	0.0831	0.0028	0.0059	0.0013	0.0026
UAN2	0.6653	0.3211	0.0898	0.0040	0.0057	0.0018	0.0033
UAN4	0.6735	0.2907	0.0844	0.0043	0.0054	0.0019	0.0029
UAN6	0.7002	0.2364	0.0799	0.0038	0.0050	0.0016	0.0028
UAN8	0.6868	0.2667	0.0827	0.0033	0.0050	0.0023	0.0030
UAN10	0.7008	0.3083	0.0857	0.0033	0.0048	0.0021	0.0029

3.2 Acid Leaching

3.2.1 Sulphuric acid route

Ajayi et al [26], reported that 60wt% sulphuric acid strength was sufficient for the optimal leaching of Kankara kaolin. Apparently, it was observed that Al_2O_3, Fe_2O_3, K_2O and Na_2O reduce progressively, while CaO and TiO_2 remained almost unchanged especially at lower reaction time. Simultaneously, SiO_2 content increased with increase in reaction time, associated with leaching of Al^{3+} ions which conforms to works of Panda et al [3]. The rate at which the silica-alumina ratio changes with respect to mode and period of kaolin treatment is depicted in Fig. 1. It can be deduced that sulphuric acid gave the highest Si/Al ratio irrespective of the treatment means.

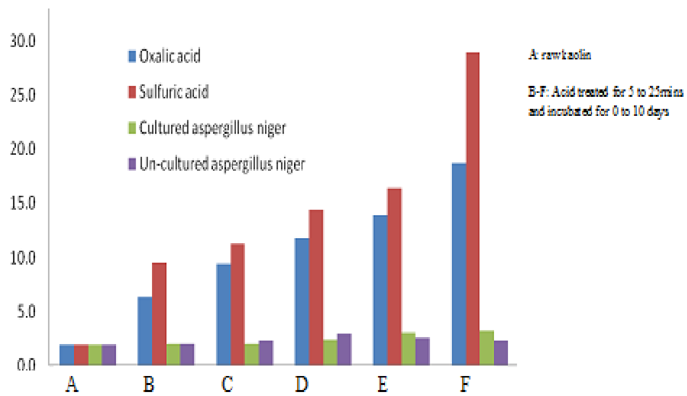

Fig. 1: Silica-alumina ratio as a function of mode of kaolin treatment

As for ferric oxide (in whatever form) it was observed that sulphuric acid was adequately digested by the chosen concentration of acid used, with a shifting order reaction, as represented in Fig. 2.

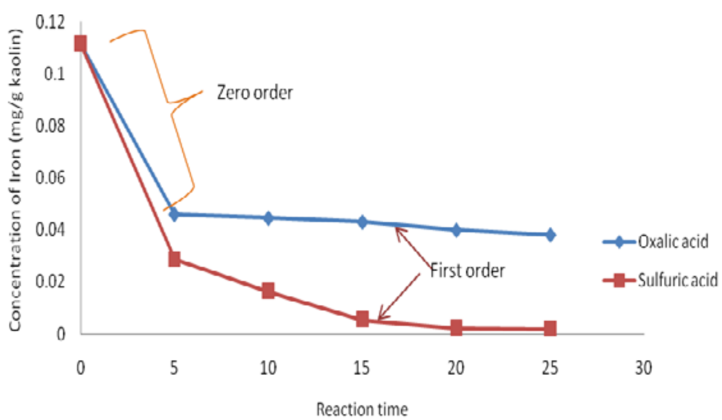

Fig. 2: Kinetic profile for iron leaching using acid

3.2.2 Oxalic acid route

As represented in Figure 3, the highest iron leaching rate was observed with 60% oxalic acid. Accordingly, this acid concentration was used subsequently in this work and the mechanism for oxalic acid leaching was observed to follow the model reported by Cameselle et al [28].

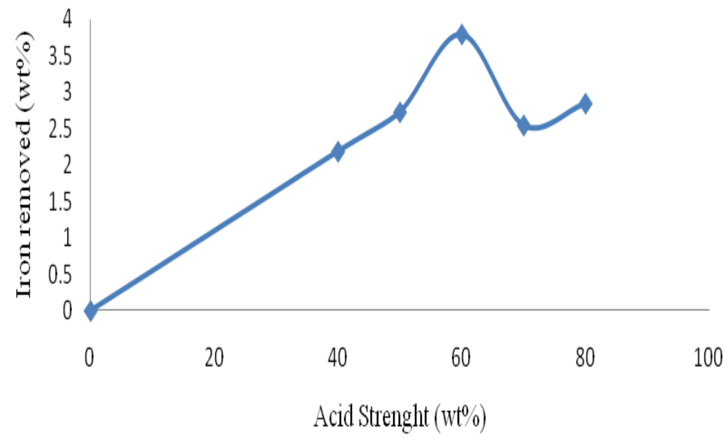

Fig. 3: Effect of oxalic acid concentration on iron removal

The observed lower rate of iron removal in Fig. 2 for oxalic acid was apparently derivable from the higher solubility of ferrous oxalate in water compared to that of $Fe_2(SO_4)_3$. Fig.1 buttresses the fact that oxalic acid is not as effective as sulphuric acid in dealumination reaction, hence the observed low Si/Al ratio.

3.3 Bioleaching

3.3.1 Cultured A.niger

The metakaolin treated with *A.niger* grown in cultured medium was observed to maintain a relatively constant Si/Al ratio and Fe^{3+} content for the first 6 days of incubation, as represented in Fig. 4. This was explained by the fact that microorganisms tend to adapt to new environment, prior to performance, i.e. release of the required quantity of organic acid for acidolysis reaction. A similar statement was made by Hosseinni et al [4] when it took *A.niger* used by them 15 days for adaptation. It is worth mentioning that majority of the iron removed resulted from the chelating and complexing action of basically the oxalic acid [11].

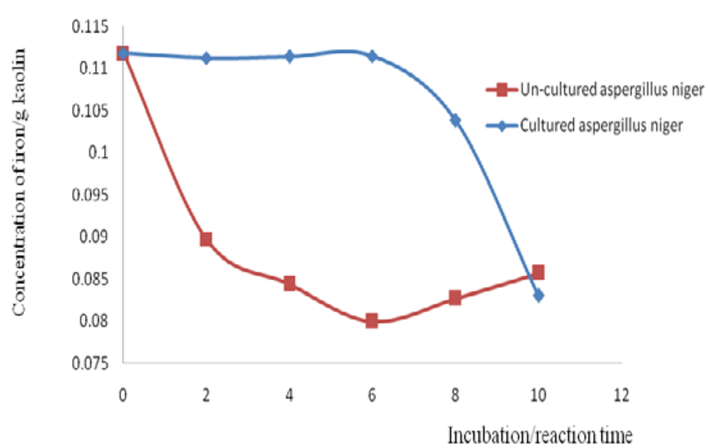

Fig. 4: Iron leaching using *aspergillus niger*

3.3.2 Un-cultured A. niger

The un-cultured *A.niger* used to leach metakaolin was observed to marginally increase the Si/Al ratio on the 3rd and 4th day of incubation, while the Fe^{3+} was noticed to drop considerably and progressively from 2nd to 6th day. After this an increase in Fe^{3+} concnetration was observed, which might have resulted from the depleted activity of the enzyme on the 6th day and residual un-solubilized complex. The speculation given for the initial enhanced Fe^{3+} reduction, was that the inherent kaolinite based microorganism in conjunction with *A.niger* worked jointly to facilitate the removal, on one hand. Shelobolina et al [29] reported that their exist microorganism in kaolin, responsible not only for iron removal, but sulfate-reducing bacteria, fermentative and denitrifying bacteria. On the other hand, the *A.niger* could have decomposed the inherent carbon based microorganism, producing the required organic acid for bioleaching.

4.0 CONCLUSION

Kankara kaolin clay reddish in colour, arising from its rich ferric content,was subjected to acid and bio-leaching studies. It was observed that among acid leaching, use of sulphuric acid tends to facilitate an enhanced removal of impurities compared with oxalic acid. Un-cultured *A.niger* commenced leaching without adaption period, while the cultured one- took time before its activity commences. Both approaches were established to be good enough for beneficiating kaoilnite clay. Bio-leaching approach could be recommended for beneficiating kaolin with intended use in food industries and other areas with sensitivity to high acid content.

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