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# EVALUATING THE CHANGES IN SURFACE PROPERTIES OF ACID-LEACHED ILIRI CLAY

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**ABSTRACT:** *Clay from Iliri was activated using hydrochloric and sulfuric acid of differing concentrations to acquire differing acidities. The chemical compositions of the raw clay and clay activated at different acid concentrations were analyzed to investigate the extent of cation dissolution. From the* $Na_2O$ *to CaO ratio, Iliri clay is swelling sodium bentonite mixed with feldspars, illite, kaolinite and plagioclase. The Langmuir isotherms of 1-aminobutane in isohexane agitated with clay slurries showed increase in clay acidity with increase in concentration of mineral acid used to leach the clay as well as the temperature at which the clay was thermally activated prior to experimentation involving adsorption of 1-aminobutane. The values of surface acidity, nm, for acid-leached Iliri clays ranged from* $0.811 \times 10^{-3}$ $molg^{-1}$ *to* $6.7705 \times 10^{-3}$ $molg^{-1}$ *and the kinetic equilibrium constant of adsorption, K, varied from 0.07828 to 0.7233 yet the surface area, A increased from* $5.2702 \times 10^{-3}$ $m^2g^{-1}$ *to* $50.6700 \times 10^{-3}$ $m^2g^{-1}$ *. Basing on acidity, pH, elemental and mineral compositions, the Iliri clay was resolved to contain montmorillonite.*

**KEYWORDS:** Changes, Surface Properties, Acid-Leached, Iliri Clay

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## INTRODUCTION

Clays are collectively called alumino-silicates as they contain aluminium oxide and silicon dioxide as universal minerals; and are classified into phyllosilicates and layers silicates (Brindley, 1978). As early as the 1940s, the active part of a cracking clay catalyst had been described to be the Al (IV) ion and found to occupy only a small part of the surface. This active part of aluminium in four coordinate forms constitutes acidity (Ravindra-Reddy et al, 2009). The smectites have high cation exchange capacity (CEC), kaolinites have negligible CEC (Bradley and Grim, 1951). Acid activated clays exhibit significantly different surface acidity compared to their non-activated counterparts. The interactions of clay surfaces with gases or liquids relevant to adsorption and catalysis are mainly governed by acid-base interactions (Jacobs 1984; Tanabe et al, 1989). These interactions are also involved in particle sintering (Pesquera,et al; 1992). Clay minerals possess attractive properties as solid acids (Ravichandran and Sivasankar, 1997; Tanabe, 1970). Their acidities are due to active centers on the surface that exhibit Bronsted and Lewis acidities. Surface acidity governs most of the clay's interactions in many applications. There is need to be determined quantitatively in relation to structural changes during acid activation and thermal treatment of clay.

The Langmuir isotherms of 1-aminobutane in isohexane slurries showed increase in clay acidity with increase in concentration of mineral acid used to leach the clay as well as the temperature at which the clay was thermally activated. The values of acidity for Central Uganda were lower than those of clays from Eastern Uganda. Basing on acidity, pH, elemental and mineral compositions, the clays from Central Uganda were found to be kaolinites or halloysites yet Eastern Uganda clays were resolved to contain nontronite and kaolinite (Mukasa-Tebandeke et al, 2014). The results on equilibriation of 1-aminobutane with slurries of clay powders in hexane indicated that surface acidity and/or general acidity of clays increased with increase in temperature and concentration of acid used in its activation can be relied on to distinguish kaolinites from smectites.

Clays change their surface properties when leached with acids. Acid leached smectites have been used in oil industries as catalysts, filter aid and bleaching agents (Kooli and Jones, 1997). Acid-leached clays show different characteristics from their raw counter parts; for example they show higher acidity and bleaching capabilities than raw clays (Jadambaa et al, 2006).

In a study aiming at determining the surface acidity changes resulting from acid treatment of clays, a volumetric titration method was used (Benesi, 1957; Cardona-Martinez and Dumesic, 1992; Kumar et al, 1995) and acidity was expressed as milliequivalents of NaOH used per 100g of clay.

According to the concepts independently proposed by J.M. Broensted and T.M. Lowry in 1923, an acid is any hydrogen containing species which can release a proton and a base is any species that accepts a proton. The equilibrium attained is shown in equation 1;

$$HA+B \longrightarrow A^{-} + HB^{+} \quad \text{.............................................1}$$

Where HA is acid and A- is conjugate base

In the same year a different approach was proposed by G.N. Lewis, which defines an acid as any species which has an incomplete electronic grouping that can accept an electron pair to give rise to a coordination bond. The base is any species that possesses a non bonding electron pair that can be defined by the reaction in equation 2;

$$B: + A \longrightarrow B\text{-}A \quad \text{.........................................................2}$$

The interactions of clay surfaces with gases or liquids that are used in adsorption and catalysis are governed by the acid-base strengths (Jacobs, 1984; Tanabe et al, 1989).

Clay minerals have been shown to possess attractive properties as solid acids (Ravichandran and Sivasankar, 1997; Tanabe, 1970) and these surface properties are associated with acidity brought about by Broensted and Lewis centers.

The adsorption of 1-aminobutane on selected clays used in the study produced adsorption isotherms of the first class type according to the Brunauer classification (Alemdaroglu et al, 2003; Gregg and Sing, 1997). The chemical interaction between the adsorbate and surface is consistent with the Langmuir adsorption isotherm equation 3 given below.

$$c/n = (1/Kn m) + c/n m \quad \text{...........................................................3}$$

Where c is the concentration of substrate in solution that is in equilibrium with the adsorbed substrate, K is the kinetic equilibrium constant of adsorption, n is the amount of adsorbed substrate per gram of solid, and n*m* is the monolayer coverage, which corresponds to the theoretical amount of solute that covers all the sites in 1.0 g of sample.

The surface acidity of clays is strongly related to adsorptive tendencies of clays. It was reported that smectite-rich clays show greater degree of linearity of 1-aminobutane adsorption isotherms than kaolinite-rich clays (Mukasa-Tebandeke et al, 2014). In addition, the smectite-rich clays undergo greater increase in surface acidity and surface area than kaolinite-rich clays when leached in acid (Alemdaroglu et al, 2003).

The Langmuir adsorption isotherms for clays derived from volcanic sediments showed greater linearity than those from non volcanic clay sediments showing the quantity of 1-aminobutane adsorbed was expected to be a linear function of the equilibrium concentration of 1-aminobutane in the solution, theoretical adsorption maximum that measures the amine-clay binding energy (Fried and Shapiro, 1956). When concentration of adsorbate rises beyond a critical value, deviations from linearity occurr, showing that competition between free amine and adsorbed molecules for the few adsorption sites available in the clay matrices takes place (Olsen and Watanabe, 1957; Mukasa-Tebandeke et al, 2015). High surface area mesoporous titanium phosphate:synthesis and surface acidity determination (Deborah et al, 2000). A mesoporous form of titanium phosphate has been prepared by reaction between phosphoric acid solution and either titanium propoxide or titanium chloride in the presence of trimethylammonium surfactants. The surfactant can be almost completely removed by extraction using acidified ethanol. The surface area of the extracted samples depends closely on the pH of the reaction medium, and the reaction temperature, and the highest surface areas.. These hydrogen phosphate groups were shown to cause high surface acidity and surface area (Deborah et al, 2000). Acid leached smectites are applied in oil industries as catalysts, filter aid and bleaching applications (Kooli and Jones, 1997). Acid-leached clays show different characteristics from their raw counter parts; for example they show higher acidity and bleaching capabilities than raw clays (Jadambaa, 2006). For clay to bleach, it must interact with the medium in which the materials or impurities to be removed are present. The interactions of clay surfaces with gases or liquids that are used in adsorption and catalysis are governed by the acid-base strengths (Campello et al, 1983; Jacobs, 1984; Tanabe, et al, 1989). The adsorption of 1-aminobutane on selected clays used in the study produced adsorption isotherms of the first class type according to the Brunauer classification (Alemdaroglu et al, 2003; Gregg and Sing, 1982). The surface acidity of clays is strongly related to adsorptive tendencies of clays. It is on this ground that determination of surface acidity of raw and acid-leached clays have to be determined. It is one of the aims of this study to determine the surface acidity of Iliri clays.

The changes in surface properties like acidity of clays from Iliri have never been published, so the objectives of this study is to evaluate changes in surface acidity, pH, composition and color of Iliri clay when leached in acid. The factors that have made clay and clay mineral to be used extensively as adsorbent in the purification of vegetable oils include its low cost, local availability and effectiveness. The textural characteristics and surface chemistry play important roles in the bleaching earth performance. The texture and surface properties of clays can be activated through acid or alkali leaching, and organic, thermal or pillaring (Farihahusnah et al, 2011).

## MATERIALS AND METHODS

### Sampling

Clay samples were collected from Iliri road swelling clay. The clay was dug and collected at depths in the range of 35 – 150 cm from the surface to minimize effect of weathering and contamination.

### Preparation of clays

Raw samples of clays were separately soaked, stirred to dilute slurry in distilled water, sieved to pass through a mess $5.3 \times 10^{-4}$ m diameter, dried at 105°C and ground to powder using a rolling mill. The clay powders were stored for future use in desiccators.

### Determining pH of clay

Weighed clay powder (1g) was placed in a beaker, water (20mL) added. The mixture was stirred continuously and allowed to equilibrate for 30 minutes at 25°C. A calibrated pH-meter was then used to read the pH of the solution. The method was repeated thrice to get comparing results .whose average was recorded

### Leaching of clays

Clay powder (100g) was mixed with acid (500mL) of appropriate concentrations (5, 10, 20, 25 % v/v) using hydrochloric and sulfuric acid in a flask separately. The mixture was heated at 105°C for 4 hours; then cooled and filtered. The residue was washed to neutrality with distilled water; then dried at 105°C in the thermo-stated oven. The dried leached powders were labeled A1, A2, A3 and A4 for the HCl-activated and B1,B2,B3 and B4 for $H_2SO_4$-activated and stored for future use.

### Determination of surface acidity of clays

Activated clay powder (0.2g) was placed in a flask. $1.0 \times 10^{-2}$M 1-aminobutane solution in isohexane (20mL) was added. The flask was stoppered and shaken vigorously for 20 hours using an electric shaker at room temperature. The equilibrium mixture was filtered. Portions of the filtrate (5.0 mL) were pipetted to a clean flask, extracted with water (5.0mL); methyl orange indicator (2 drops) added and the mixture titrated with 0.004M hydrochloric acid to orange endpoint (Benesi, 1957; Benesi, 1978; Cardona-Martinez and Dumesic, 1992; Kumar et al, 1995). For each clay sample activated at a particular temperature, four entries were entered as a result of the leaching medium. Each clay type was activated by heating at different temperatures in the range between 40 and 80°C at internals of 10°C from each temperature used. Each analysis was carried out thrice to get comparing results. The data obtained was averaged.

## RESULTS AND DISCUSSION

### Location and geological settings of sampled clays

Iliri is located in Bokora Corridor Wildlife Reserve, which lies between Toror and Napak mountains in North Eastern Uganda's Karamoja region. The raw swelling clay from the deposit in Iliri was collected from the roadside from Katakwi to Moroto from a ditch 35 cm deep to minimize contamination and weathering effects.

## Sampling methods

The samples were collected at depths in range of 35 – 150 cm from the surface to minimize the effect of weathering and contamination.

## Composition of clays

The chemical analysis of sample was carried out and the data were presented in Table 1. In a study involving clays, it is important to establish the elemental constitution of the solid because surface and bleaching properties of clays and clay material depend on the elements present. The averaged data obtained in the elemental analyses of Iliri clays is shown in Table 1.

**Table 1: The average chemical composition of the raw clay**

| clay | component | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ | LOI |
|---|---|---|---|---|---|---|---|---|---|
| Iliri | % | 46.7 | 15.9 | 7.8 | 1.5 | 2.0 | 3.8 | 1.3 | 14.5 |

Iliri clay had high silica content showing presence of quartz in the mineral mixture. The high quartz content suggests that the clay had been transported via erosion fro where it was mined. The clays from magmatic sediments in oceans were reported to contain major elements with relatively high magnesium oxide, ranging from 23.9 to 40.4 % and low silicon dioxide and aluminium oxide, ranging from 12.8 to 29.0% (Herzig et al, 1998) . However, clays from Iliri are associated with volcanic margins of Toror and Napak mountains. The loss on ignition (LOI) of the Iliri clay was 14.5% showing that clay may have suffered structural changes including dehydration, dehydroxylation and decomposition of volatile carbonates upon heating clays to 105°C (Ball, 1964). The ratio of $Na_2O$ to CaO was 1.2, a value greater than 1, which is indicative of the presence of swelling bentonite (Basim, 2011; Usman et al, 2012). Therefore, the clay was classified as sodium bentonite or montmorillonite. The concentration of hydrochloric and sulfuric acid used to leach the clay was varied from 0 to 30%, to optimally attack the interlayer cations and octahedral ions, replace them with hydrogen ions (Didi et al, 2009; Ujeneza et al, 2014). The extent of removal of octahedral ions would influence the surface properties of the clay skeleton left behind. The leached needed to be washed to neutrality to expel free mineral acid. Retention of acid in the clay matrix should lead to excessive surface acidity (Beneke and Lagaly, 2002; Mukasa-Tebandeke et al, 2014). If the clay is washed with distilled water to neutrality, acidity would result from silica hydrate or hydroxyl groups on the surface of the clay minerals. Hence the surface acidity of clays depend mainly on amount of hydrated silica present in the matrix. Surface acidity was shown to increase with concentration of acid and temperature of activation by several authors (Alemdaroglu et al, 2003; Motlagh et al., 2011., Mukasa-Tebandeke et al, 2015., Ujeneza et al, 2014). Reacting natural clays or silicates with sufficiently strong acids leads to formation of silica which strongly reduces the cation exchange and increase clarifying effects. Silicates have to be reacted with acid until they are decomposed to silica to a large extent. Acid activation of Iliri clay modified the structure of the clay and this was indicated by the change in the chemical composition given in Table 2. Both hydrochloric and sulfuric acid destroyed the structure of the clay to nearly the same extent.

**Table 2:** Chemical composition of raw and acid leached Iliri Clay

| %oxide | Raw | 5% $H_2SO_4$ | 10%$H_2SO_4$ | 20% $H_2SO_4$ |  | 30%$H_2SO_4$ | 5%HCl | 10% HCl | 20% HCl | 30%HCl |
|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 46.7 | 52.1 | 60.0 | 67.2 |  | 71.5 | 54.2 | 61.0 | 68.2 | 71.8 |
| $Al_2O_3$ | 15.9 | 14.5 | 13.7 | 7.0 |  | 6.8 | 14.1 | 13.5 | 7.0 | 6.8 |
| CaO | 4.0 | 0.6 | 0.5 | 0.5 |  | 0.5 | 0.5 | 0.5 | 0.4 | 0.4 |
| MgO | 1.5 | 0.4 | 0.4 | 0.3 |  | 0.3 | 0.4 | 0.4 | 0.3 | 0.3 |
| $Na_2O$ | 3.8 | 1.0 | 0.9 | 0.7 |  | 0.7 | 0.9 | 0.9 | 0.7 | 0.7 |
| $K_2O$ | 1.3 | 1..1 | 1.1 | 1.0 |  | 1.1 | 1.1 | 1.1 | 1.0 | 1.1 |
| $Fe_2O_3$ | 7.8 | 4.2 | 4.0 | 1.5 |  | 0.8 | 4.0 | 3.7 | 1.2 | 0.8 |
| LOI | 14.5 | 17.6 | 17.5 | 16.3 |  | 11.0 | 16.8 | 16.5 | 16.3 | 10.0 |

Silicon dioxide content of leached Iliri clay rose from 46.71% to 71.8 % as concentration of acid used was increased from 0 to 30%. The content of other elements decreased after activation. The increase in Silica content and concentration decrease the for other oxides was in agreement with the results reported by several authors (Ujeneza et al, 2014., Usman et al, 2013 and Arfaoui et al, 2010). The octahedral sheets got destroyed as the exchangeable cations dissolved in the acid while the silica generated by the tetrahedral sheet remained in the solid phase due to its insolubility (Diaz and Santos, 2001) so increasing silica content. Acid-leaching of clays enhances bleaching power of silicates for oils, waxes, paraffins by transforming silicic acid of natural silicates to hydrated silica (Beneke and Lagaly, 2002). This too increases surface acidity. Similarly, a fine bentonite suspension put in contact with sulphuric acid at various temperatures between 60 and 120 $^{o}$C for durations between six and twelve hours is known to yield bleaching clay on being washed to neutrality with distilled water (Didi et al, 2009; Kamal et al, 2011). Athi River bentonite was activated using sulphuric acid at various acid concentrations, clay acid ratio, temperature and contact times and both cation exchange capacity and the apparent bulk density were found to decrease with increase in acid concentration yet bleaching efficiency increased (Ujeneza et al, 2014).

## Variations in pH of clay slurry with leaching in acid

The pH of clays commonly suggests presence of characteristic elements upon which prediction of surface and bleaching properties can be made. Record of average pH of clays may serve as reference to nature of the environment from which the clay sediments were collected or formed. The pH of raw and acid-leached clay from Iliri were determined and recorded in Table 2.

**Table 2:** pH of aqueous clay slurries

| Clay | A0 | A1 | A2 | A3 | A4 | B1 | B2 | B3 | B4 |
|---|---|---|---|---|---|---|---|---|---|
| pH | 8.4 | 6.7 | 6.5 | 5.1 | 5.8 | 6.5 | 6.1 | 5.5 | 4.8 |

The determination of pH of clay slurries in distilled water was repeated thrice and the average of the three values has been tabulated in Table 2 above. Readability of pH was 0.04.

The average pH of raw Iliri clay was 8.50 ± 0.034 because the environment from which it was mined was ultra basic. The alkalinity of the clay slurries is attributable to presence of alkali and alkaline earth metals whose aqueous silicates strongly hydrolyze raising the pH above 7. This confirmed presence of excess alkali metals like sodium and potassium as well as K-feldspars in the clay. The pH of slurries for bentonites or montmorillonites was reported to lie in the range between 7.8 and 8.5 (Hamza, A. (1966) Noyan et al, 2006; Sarikaya et al, 2007; Sarikaya et al, 2000). So Iliri clay is a high smectite content. Generally the pH of the clay slurry in distilled water decreased with increase in concentration of acid used to leach the clay because leaching removed interlayer lamellar cations in the bentonite. Removal of these cations reduces the extent to which the aluminosilicate would hydrolyze anionically, so liberating fewer and fewer hydroxide ions which would raise pH. At concentration of acid higher than 5%, the pH of the slurry became less than 7 showing that the clay turns into a weak acid. The weak acid ionizes to produce few hydrogen ions which lower the pH below 7. The pH of the slurries decreased with increase in mass percent of acid used.

## Color

Colored clays have interlayer cations as $Fe^{2+}$, $Fe^{3+}$, $Mn^{2+}$, $Ti^{4+}$ and other transition metal ions. These interlayer octahedral ions are easily replaced by protons during acid activation using low or moderate concentrations of the acids (Beneke, and Lagaly, 2002; Fahn, 1976) to give silica to a large extent. The clay deposits sampled exhibited different colors depicting differences in composition of trace transition elements composition in the clays. The appearance of clay depends on the quantity and oxidation state of iron and other transition elements present. While clays containing iron in oxidation state +3 are yellow or brown. Green clays contain iron in oxidation state +2 but color can also arise from presence of manganese and titanium compounds in different oxidation states (Beneke and Lagaly, (2002); Fahn, 1976; Nyakairu and Koeberl, 2001). The Iliri clay appeared pictch black due to presence of iron and other transition metal ions in different oxidation states as well as difference in the mineralogical compositions. Color alone cannot be based on to assert the composition of smectites. The clay changed from black to near white as the concentration of acid used to leach it increased due to removal of interlayer cations on leaching. Among the octahedral ions removed from the lamellar are transition metal ions which are intensely colored. Since removal of the octahedral ions left a silicon dioxide skeleton, the gradual change of color from grey black to white signified the destruction of crystal structure of the clay by acid corrosion.

## IR spectra of clays

Infrared spectroscopy may give chemical overview of a sample, with all the chemicals present contributing to the spectrum produced. The method can be used to qualitatively analyze a variety of samples ranging from biological samples to clay minerals. The spectrum in Figure 1 is for clay from Iliri. It consists of several peaks at different frequencies.

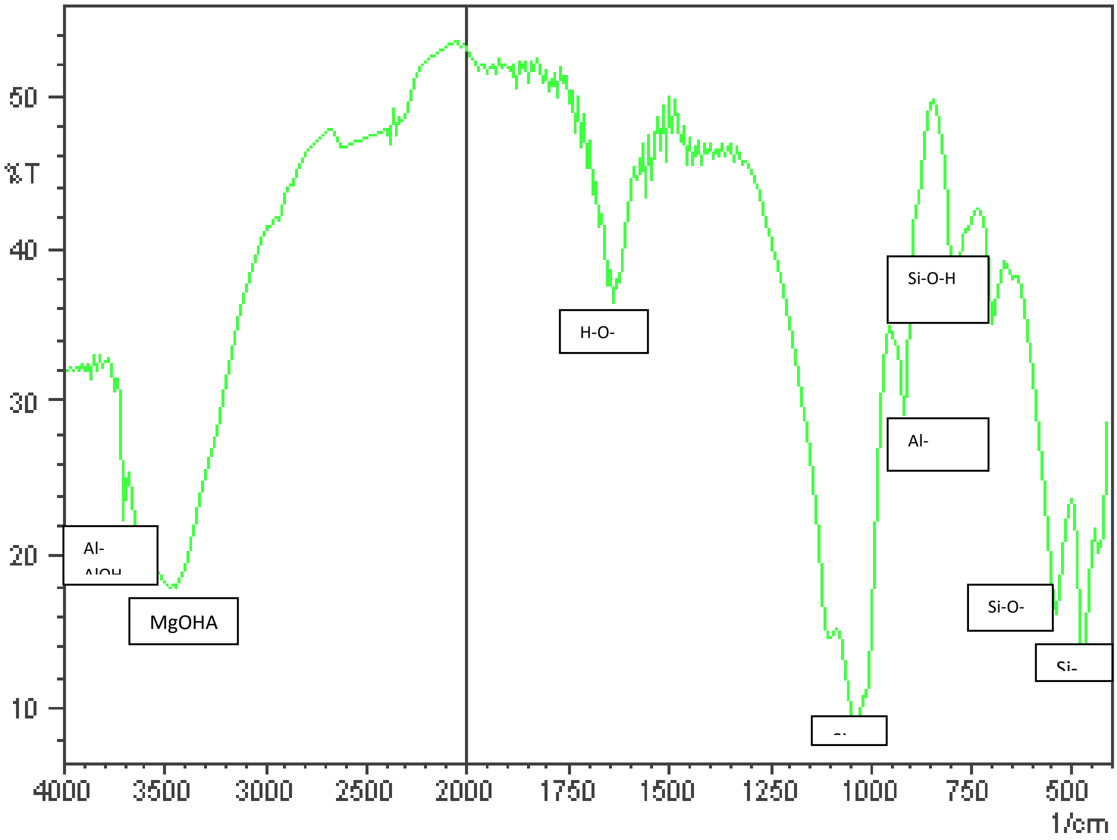

Figure 1: IR spectrum for Iliri clay

The band at 1040 $cm^{-1}$ has been assigned to (Si-O). The band at 3454 $cm^{-1}$ was due to adsorbed water, and that at 3640 $cm^{-1}$ was due to (Al-Al-OH, Mg–OH–Al). The absorption bands at 918 and 879$cm^{-1}$ in were obscured by Si-O mode which broadened. These bands are due to the bending mode of Al-Fe-OH bonds and smectites are also expected to show absorption bands at 845$cm^{-1}$ (Brigatti et al, 2006; Christidis et al, 1995). Some absorption peaks were not well resolved because the different clay minerals were mixed together.

**IR** for clay leached in 25% acids

### Surface acidity of raw and acid leached clay from Iliri

It is known that bleaching earths must operate optimally so as to remain affordable. So producers of bleaching clays control surface acidity to guarantee the highest degree of activity (Mag, 1990) with the aim of avoiding hydrolysis of triglycerides by the acid catalysts in presence of moisture originating from the oils or the bleaching clay.

The standard clay suspension in isohexane and standard solution of 1-aminobutane or aminocyclohexane in isohexane if mixed, followed with determination of free amine concentrations at equilibrium titrimetrically or spectrophotometrically (Alemdaroglu et al, 2003; Benesi, 1957; Cardona-Martinez and Dumesic, 1992; Drushel and Sommers, 1966; Kumar et al, 1995) gave data on acidity of the clay.

As the surface acidity of the clays and clay minerals have been found to be due to Lewis and Broensted acidities, (Alemdaroglu et al, 2003; Campelo et al, 1983; Mokaya, 2001) and found to be closely related to the bleaching capacity (Mills et al, 1950) and cracking capability. It was necessary to determine the acidity of acid-leached clays used in this study in order to determine the direction of change in acidity when montmorillonite is leached with acid. The surface acidities of clay samples were determined using 1-aminobutane on the basis that adsorption 1-aminobutane was irreversible.

As far back as the 1960s, 1-aminobutane dissolved in isohexane was directly titrated on clay suspensions in isohexane using bromothymol blue and bromocresol green as indicators (Drushel and Sommers, 1966). It was reported that 1-aminobutane was successfully determined using methyl orange indicator when distinguishing acidity of kaolinites and smectites (Mukasa-Tebandeke et al, 2015). In this study, 1-aminobutane, pkb = 10.9; kb = $1.26 \times 10^{-11}$ $moll^{-1}$, was used as a base to determine the total acidity of the differently acid-activated clay powders from Iliri, North Eastern Uganda.

The mixture of the 1-aminobutane in equilibrium with the strongly agitated clay–amine mixture showed that surface acidity of selected clays increased with increase in the concentration of the acid used to leach the clay as well as increase in temperature at which the clay was activated. This has been shown by the decrease in the quantity of 0.04M hydrochloric acid required to react with the 1-aminobutane in equilibrium with the clays baked separately at 40, 50, 60 and 70°C.

As the leached clays are probably in the acid-form of ion-exchange resin, the 1-aminobutane binds to the clay surfaces either by reacting with the available protons on the surface of the clay or by sharing the lone pair or non-bonding pair of electrons on the nitrogen with the vacant sites on the clay surface. So the surface acidity determined by adsorption of 1-aminobutane corresponds to the determination of both Lewis and Broensted acidities together.

The titre of hydrochloric acid reacted with 1-aminobutane remaining in solution at equilibrium decreased as the concentration of the acid used to leach the clay increased as well as the temperature of thermal activation increased. This showed that the acidity of the clays increased. The decrease in concentration of 1-aminobutane in $100cm^3$ of 0.04molar solution when shaken to equilibrium with 1g of clay was calculated and recorded in Table 3.

**Table 3**: Molar concentrations x $10^{-3}$ of 1-aminobutane at equilibrium

| | A1 | A2 | A3 | A4 | B1 | B2 | B3 | B4 |
|---|---|---|---|---|---|---|---|---|
| 40 | 5.38 | 4.90 | 1.90 | 1.60 | 3.65 | 3.50 | 3.00 | 2.40 |
| 50 | 4.20 | 3.95 | 1.60 | 1.30 | 2.65 | 2.60 | 1.50 | 1.20 |
| 60 | 3.60 | 2.30 | 1.30 | 1.00 | 1.35 | 1.65 | 1.10 | 0.90 |
| 70 | 2.60 | 2.10 | 0.80 | 0.20 | 0.70. | 0.30 | 0.20 | 0.10 |

For all the clays tested there is decrease in quantity of free 1-aminobutane as both concentration of acid and temperature of activation because the acidity of the clay increased as temperature of activation and concentration of acid increased. This is shown by decrease in concentration of 1-aminobutane in equilibrium mixture formed after agitating the clay with the amine, shown in Table 3.

The data in Table 3 above shows that there was a strong relationship between the quantity of 1-aminobutane adsorbed per gram of clay, temperature at which the clay is activated and the concentration acid used in the leaching clays. It was suggested that the increase in Broensted acidity was due to the protons of the hydroxyl groups at the corners of the octahedral sites which become more labile because of structural deformation caused by acid-leaching (Alemdaroglu et al, 2003; Ravichandran and Sivasankar, 1997; Tanabe, 1970; Tanabe et al, 1989). The increased acidity upon leaching the The relation suggests that the acid-leaching increased the number acid sites in the clay mineral by the removal of exchangeable cations like $Ca^{2+}$ and/or $Na^{+}$ which lie between the clay layers (Jacobs, 1984). When the protons in the acid used to leach the clay replaced the exchangeable ions, Lewis acidity of the clays increased. This led to increased adsorption of 1-aminobutane on clay suspensions used. However, although removal of octahedral ions like $Mg^{2+}$ and $Al^{3+}$ occurred during the leaching of the clays samples, it has been observed that protons from the acid cannot fill in the empty spaces left (Alemdaroglu et al, 2003) so the octahedral clay with acid must be due to the octahedral vacancies left in the clay lattices (Benesi, 1957; Cardona-Martinez and Dumesic, 1992; Kumar et al, 1995).

Calculations for the molar concentration of 1-aminobutane present in solution in equilibrium with the adsorbed molecules per gram of clay used were computed and recorded in Tables 4a and 4b. The results in Tables 4a and 4b show that the acidity increased with increase in temperature and concentration of acid because more acid sites became available as a result of corrosion or heating. The data in Tables 4a and 4b was plotted to give Figures 3a-3h which verify Langmuir adsorption isotherms. The plot of surface acidity, n, versus the concentration, c, of the 1-aminobutane in equilibrium with clay material gave straight line graphs in Figures 3a-3h. All acid-leached Iliri clays studied at different temperatures obeyed Langmuir isotherms during the interaction between the 1-aminobutane and clays. The representative plot of n versus c is shown in Figures 3a-3h revealed that surface acidity of clay materials used in this study increased with increase in both temperature and concentration of acid used to leach the clay because increase in temperature favored dissociation of water of crystallization in the clay exposing more hydroxyl groups. The surface acidity of all clays studied increased as temperature of activation and strength of acid increased showing that replacement for metal ions had been effective. The increase in acidity of clays is shown by the positive slopes of the graphs as shown in Figures 3a-3h (Alemdaroglu et al, 2003).

**Table 4 a:** Langmuir data on adsorption of 1-aminobutane on Iliri clays

| Temp /$^oC$ | A1<br>n | c | n/c | A2<br>n | c | n/c | A3<br>n | c | n/c | A4<br>n | c | n/c |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 40 | 5.28 | 2.30 | 2.29 | 5.35 | 2.40 | 2.23 | 6.5 | 2.90 | 2.24 | 7.25 | 3.20 | 2.27 |
| 50 | 5.80 | 2.50 | 2.32 | 6.0 | 2.60 | 2.31 | 7.25 | 3.10 | 2.34 | 8.1 | 3.30 | 2.45 |
| 60 | 6.40 | 2.70 | 2.37 | 7.10 | 3.10 | 2.29 | 8.00 | 3.35 | 2.39 | 8.9 | 3.40 | 2.61 |
| 70 | 7.50 | 2.95 | 2.54 | 8.10 | 3.20 | 2.53 | 9.0 | 3.70 | 2.43 | 9.40 | 3.50 | 2.69 |

**Table 4 b:** Langmuir data on adsorption of 1-aminobutane on Iliri clays

| Temp/ $^oC$ | B1<br>n | c | n/c | B2<br>n | c | n/c | B3<br>n | c | n/c | B4<br>n | c | n/c |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 40 | 6.40 | 3. | 2.13 | 6.5 | 3.10 | 2.10 | 6.8 | 3.2 | 2.13 | 6.9 | 3.3 | 2.1 |
| 50 | 7.40 | 3.2 | 2.31 | 7.60 | 3.25 | 2.34 | 7.80 | 3.35 | 2.33 | 7.85 | 3.4 | 2.3 |
| 60 | 8.30 | 3.5 | 2.37 | 8.40 | 3.40 | 2.47 | 8.70 | 3.6 | 2.42 | 8.9 | 3.7 | 2.4 |
| 70 | 8.90 | 3.6 | 2.47 | 9.30 | 3.70 | 2.51 | 9.50 | 3.9 | 2.44 | 9.7 | 4.0 | 2.45 |

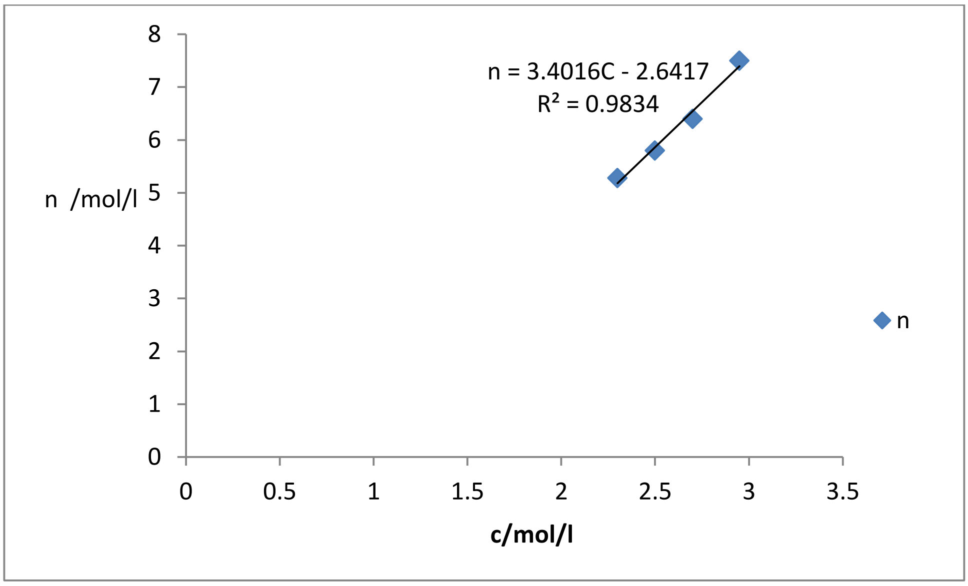

**Fig 3a**

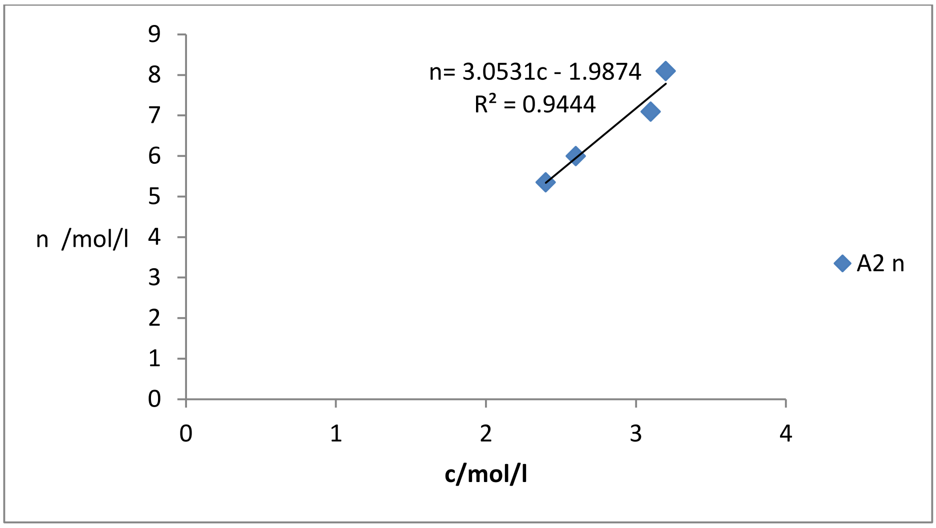

**Fig 3b**

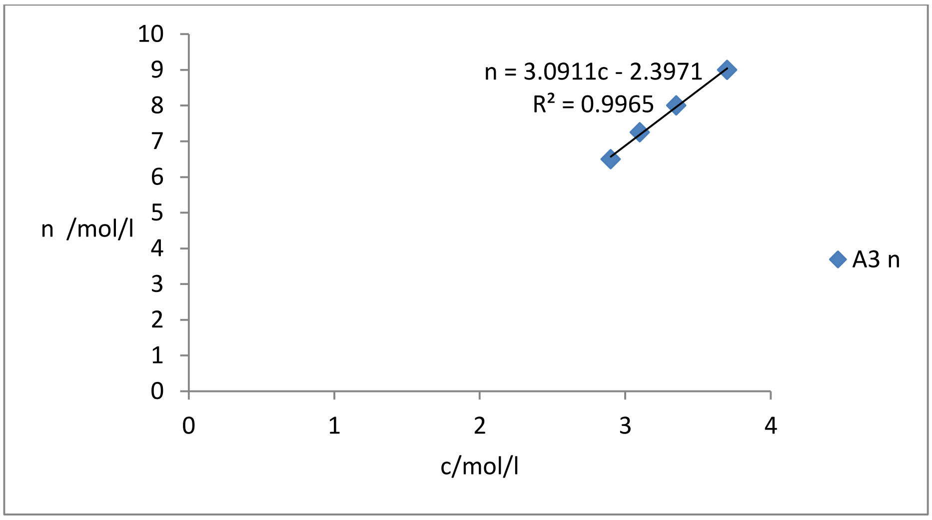

**Fig 3c**

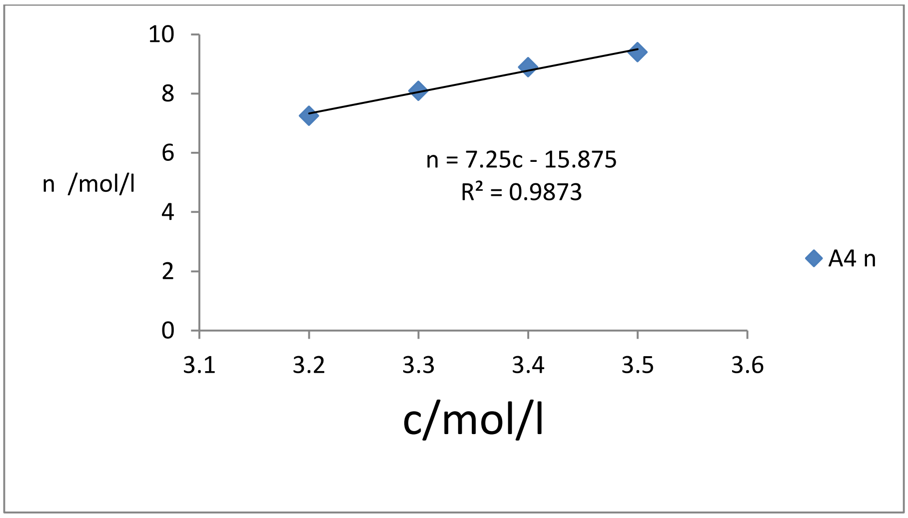

**Fig 3d**

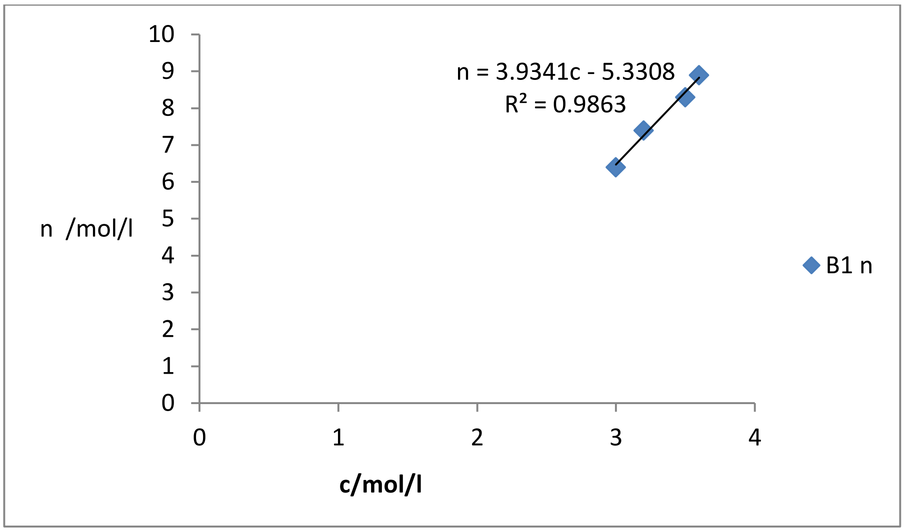

Fig 3e

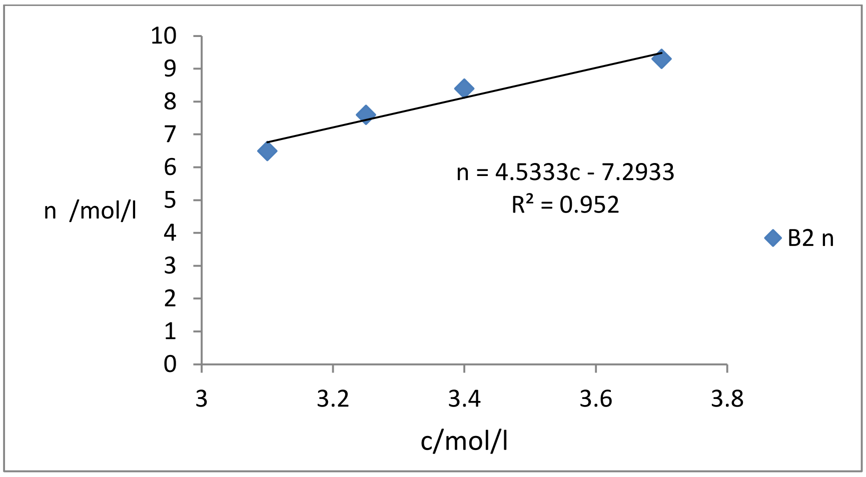

Fig 3f

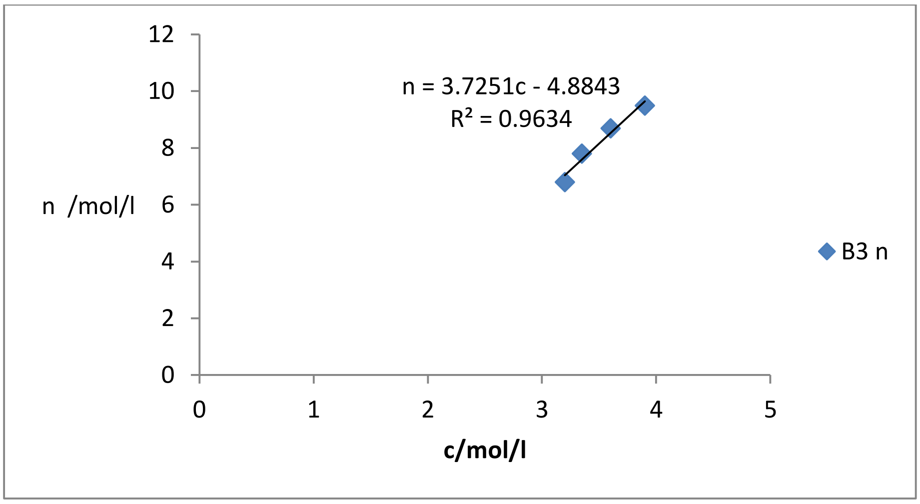

Fig 3g

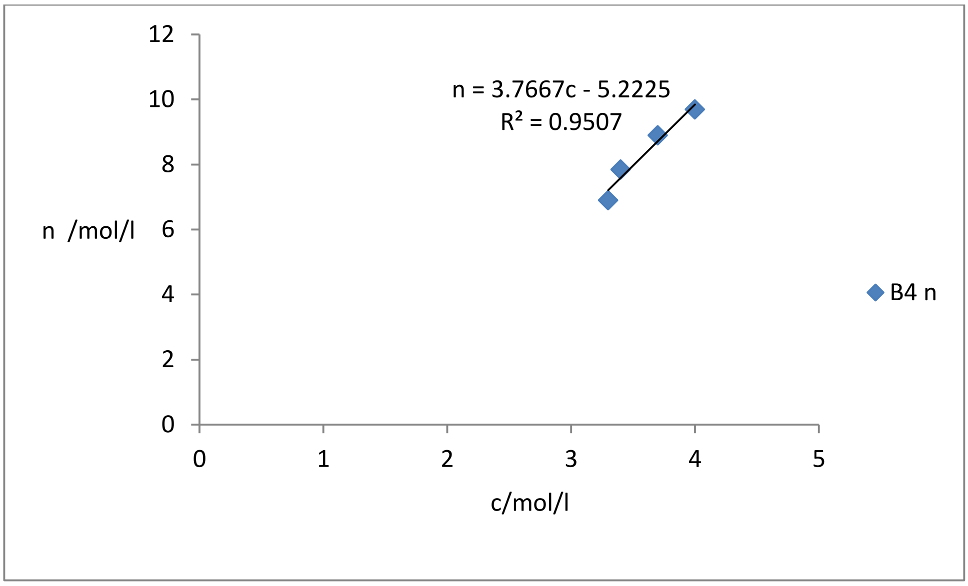

**Fig 3h**

**Figure 3**: Representative Langmuir adsorption isotherms for 1-aminobutane on different Iliri clays

The increase in amount of 1-aminobutane adsorbed per gram of clay with increase in both concentration of acid used to leach the clay and temperature at which the clay material was activated is explained in terms of increase in number of acid sites created in the clay materials. The increase in slopes of the Langmuir isotherms with increase in concentration of acid used has been used to suggest that acidity increased. The Langmuir equations derived from each plot were as shown below:

$n = 3.4016c - 2.6417$, $R^2 = 0.9834$ for A1.

$n= 3.0531c - 1.9874$, $R^2 = 0.9444$ for A2.

$n = 3.0911c - 2.3971$, $R^2 = 0.9965$ for A3.

$n = 7.25c - 15.875$, $R^2 = 0.9873$ for A4.

$n = 3.9341c - 5.3308$, $R^2 = 0.9863$ for B1.

$n = 4.5333c - 7.2933$, $R^2 = 0.952$ for B2.

$n = 3.7251c - 4.8843$, $R^2 = 0.9634$ for B3.

$n = 3.7667c - 5.2225$, $R^2 = 0.9507$ for B4.

The Langmuir adsorption isotherms for the Iliri clays were greatly linear and their $R^2$ value ranged from as low as 0.9444 $\pm$ 0.01 to as high as 0.9965 $\pm$ 0.01. The acidity of clays was strong, so their capacity to bind 1-aminobutane was high as they could not reach the saturation point easily (Nodvin et al, 1986). The deviation from linearity was explained as arising from adsorption beyond a monolayer which leads to competition between adsorbate molecules (Langmuir, 1916). It was noted that non linearity can result from overcrowding at very high concentrations of adsorbate molecules leading to steric interference (Hundal, 1988). The limiting factor is thermodynamic instability of highly concentrated sample zones which leads to viscous fingering effects (Hundal, 1988).

For all the clays tested for acidity under different conditions of temperature and concentration of acid used to activate the clay, the slopes for the Langmuir isotherms were positive showing that acidity and surface areas increased with increase in both temperature and concentration of acid used (Alemdaroglu et al, 2003). The acidity of bleaching clays depends on the degree of activation, the higher the degree of activation, the higher the degree of cation substitution in the structure inter lamellar layers by hydrogen ions of the acid used for its activation (Alemdaroglu et al, 2003; Campelo et al, 1983; Drushel and Sommers, 1966). That is why smectite-rich clays leached with 20% acid had higher acidity than those leached with 5% acid. The leached clays should show a maximum increase in n at 40% acid (Alemdaroglu et al, 2003).

The acidity values obtained in these experiments were less than expected from literature (Alemdaroglu et al, 2003; Campelo et al, 1983) because the clays used in the current study were not pure. The increase in acidity with increase in concentration of acid used to leach the clays showed that Lewis acidity greatly increased. It can be inferred that when clay matrices are leached with acids, there is removal of octahedral exchangeable ions like $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ and $Fe^{3+}$ (Balaras et al, 1999). The removal of these ions leaves a silicon-oxygen skeleton with octahedral vacant sites. As smectites contain more octahedral ions than kaolinites it has been suggested that clays which showed lower acidity were kaolinites and the ones that attained higher acidity on acid-leaching were smectites. As the concentration of acid used to leach the clay increased, the number of octahedral vacancies increased so acidity of the clay matrices increased.

From the plot of the amount of 1-aminobutane adsorbed per gram of clay at the particular temperature of activation plotted against concentration of 1-aminobutane in solution that is in equilibrium for the different clays, there is linear increase in quantity of amine adsorbed from solution showing that acidity increased even with the increase in temperature due dehydration. The variations in n/c versus c shown in Figures 4a -4h for the clay materials studied showed the Langmuir adsorption isotherms are valid for the adsorption of 1-aminobutane on clay materials studied. Langmuir isotherms in Figures 4a -4h have positive gradients showing that both surface areas and acidity of leached clays increased with increase in temperature and concentration of acid used to activate the clays. The acidity and surface area increased gradually for all the clays tested because the chemical reactions which took place in the structure of the clay during acid-leaching led to removal of some ions giving way to creation of octahedral vacancies in the matrix, so leading to increased Lewis acidity (Alemdaroglu et al, 2003).

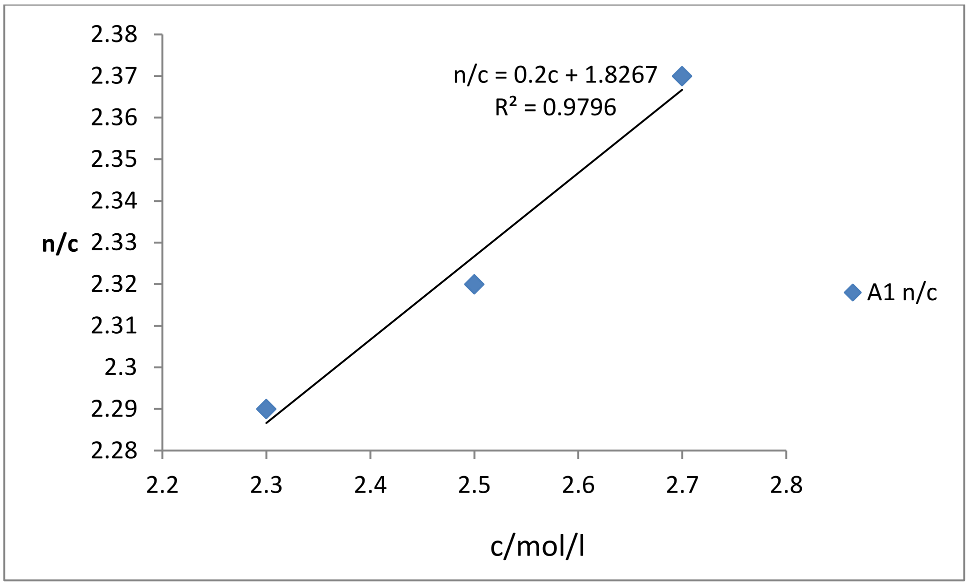
2.38
2.37
2.36
2.35
2.34
n/c
2.33
2.32
2.31
2.3
2.29
2.28
n/c = 0.2c + 1.8267
R² = 0.9796
◆ A1 n/c
2.2
2.3
2.4
2.5
2.6
2.7
2.8
c/mol/l

Fig 4a

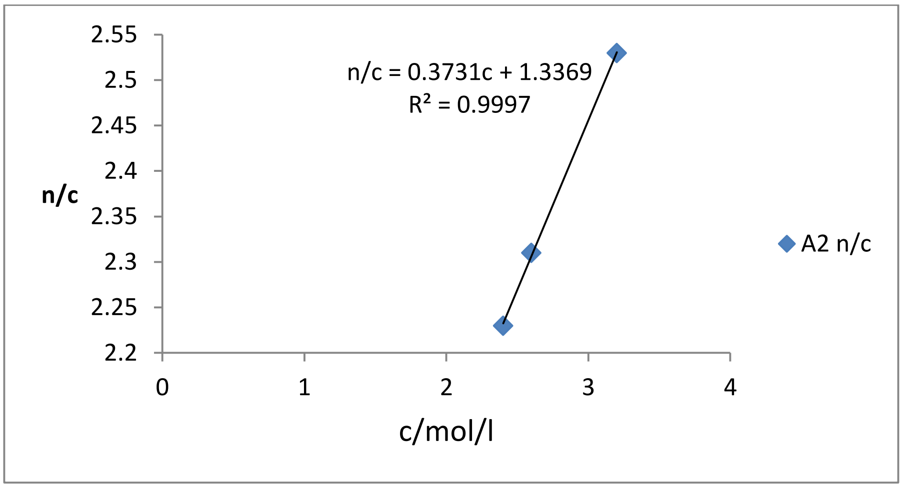
2.55
2.5
2.45
2.4
n/c
2.35
2.3
2.25
2.2
n/c = 0.3731c + 1.3369
R² = 0.9997
◆ A2 n/c
0
1
2
3
4
c/mol/l

Fig 4b

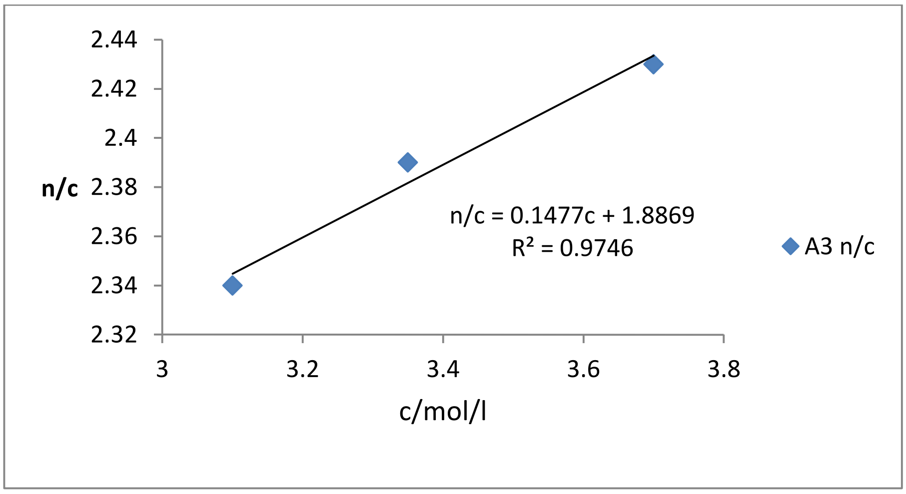
2.44
2.42
2.4
n/c
2.38
2.36
2.34
2.32
n/c = 0.1477c + 1.8869
R² = 0.9746
◆ A3 n/c
3
3.2
3.4
3.6
3.8
c/mol/l

**Fig 4c**

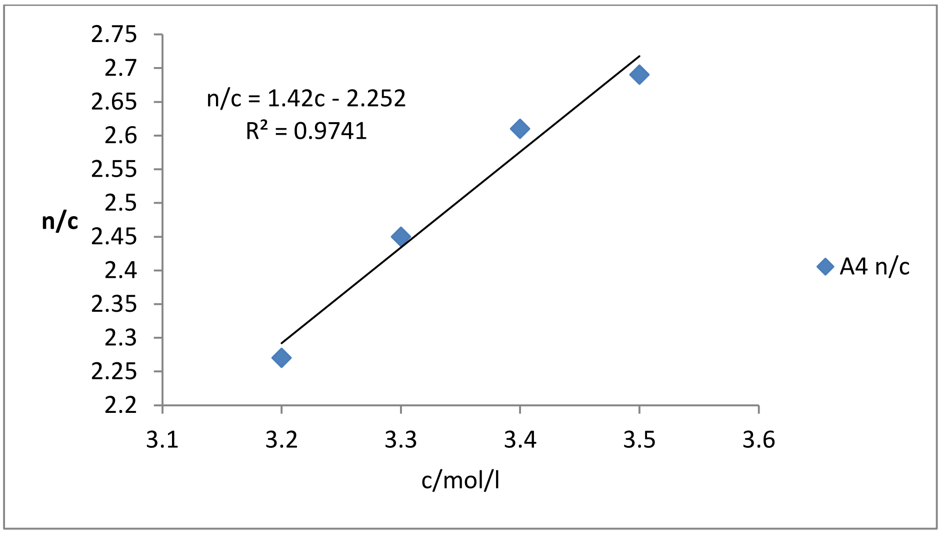

**Fig 4d**

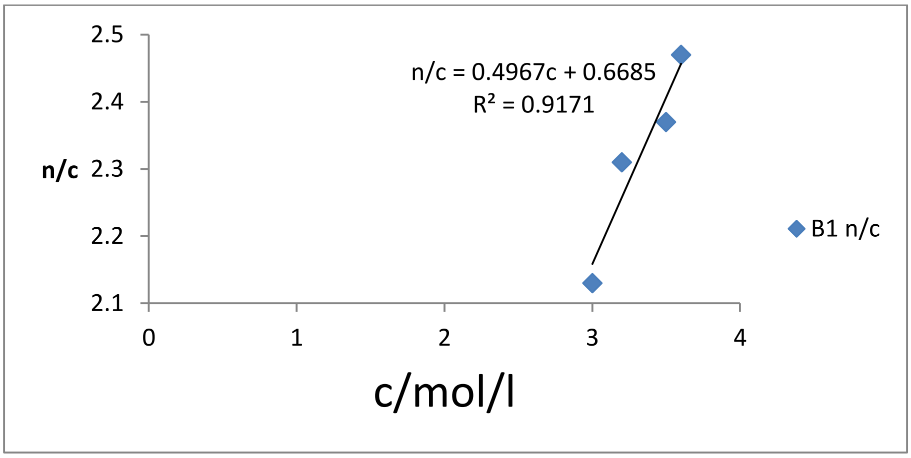

**Fig 4e**

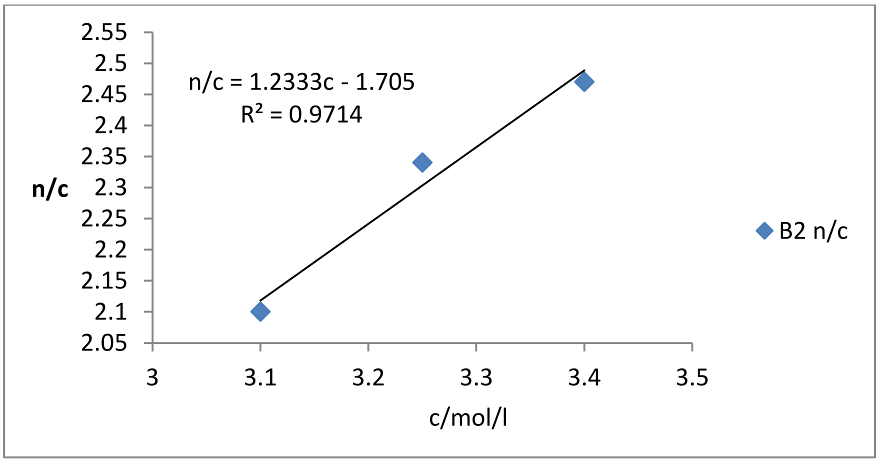

**Fig 4f**

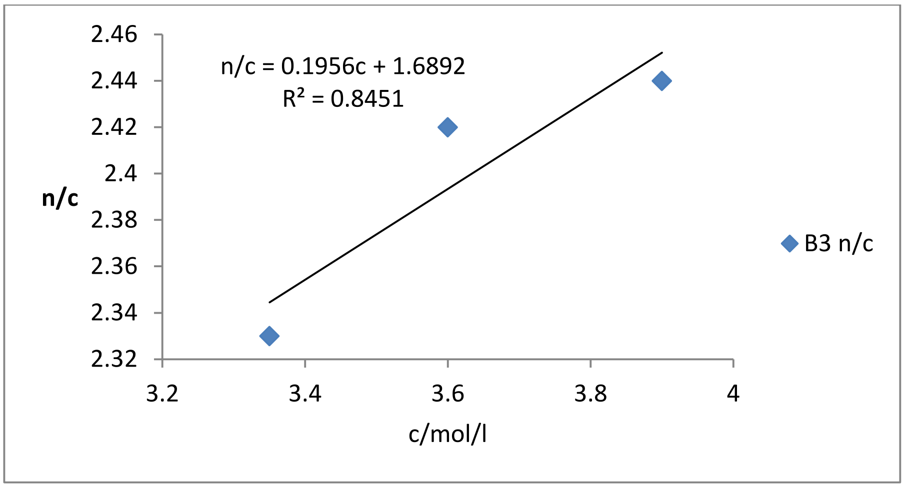

**Fig 4g**

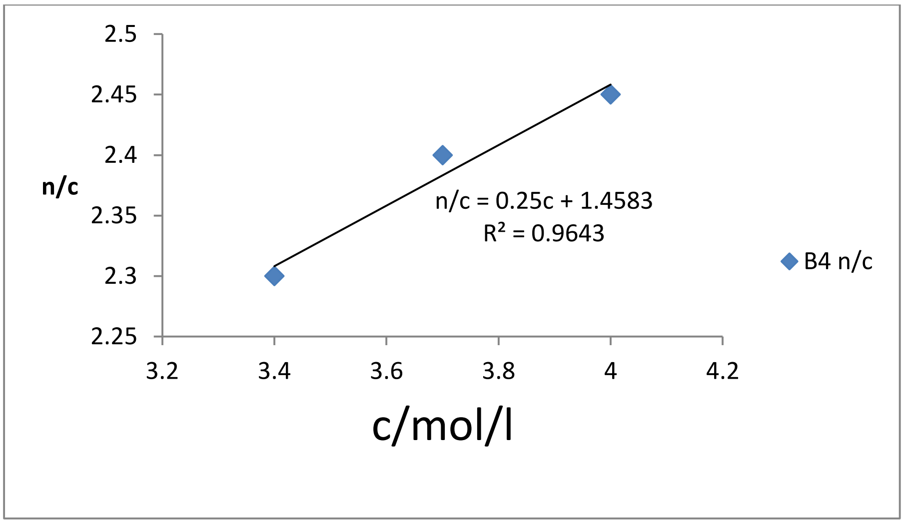

**Fig 4h**

**Figures 4a-4h:** Representative plot of n/c versus c for adsorption of 1-aminobutane on Iliri clays

The Langmuir adsorption isotherms showed surface areas of the clay materials increased on acid-leaching. The increase in concentration of acid used to leach the clay with increase in linearity of plots in Figure 4 showing that the Langmuir adsorption isotherms are valid for even clays with low smectite content because all leached clays are acidic due to hydroxyl groups.

The Langmuir equations derived from each plot were as shown below:

n/c = 0.2c + 1.8267, $R^2 = 0.9796$, $^1/_{nm}$=0.2, nm=5.0x$10^{-3}$ molg$^{-1}$, $^1/_{Knm}$= 1.8267, K=0.1095, A= 37.4197 x$10^{-3}$ m$^2$g$^{-1}$ for A1.

n/c = 0.3731c + 1.3369, $R^2 = 0.9997$, $^1/_{nm}$=0.3731, nm=2.6802x$10^{-3}$ molg$^{-1}$, $^1/_{Knm}$=1.3369, K=0.2791, A=20.0584 x$10^{-3}$ m$^2$g$^{-1}$ for A2.

n/c = 0.1477c + 1.8869, $R^2 = 0.9746$, $^1/_{nm}$ =0.1477, nm=6.7705x$10^{-3}$ molg$^{-1}$, $^1/_{Knm}$= 1.8869, K=0.07828, A=50.6700 x$10^{-3}$ m$^2$g$^{-1}$ for A3.

$n/c = 1.42c - 2.252$, $R^2 = 0.9741$, $^1/_{nm}=1.42$, $nm=0.7042\times10^{-3}$ $molg^{-1}$, $^1/_{Knm}=2.252$, $K= 0.63060$, $A=5.2702\ x10^{-3}\ m^2g^{-1}$for A4.

$n/c = 0.4967c + 0.6685$, $R^2 = 0.9171$, $^1/_{nm}= 0.4967$, $nm=2.0133\times10^{-3}$ $molg^{-1}$, $^1/_{Knm}=0.6685$, $K=0.7430$, $A= 15.06517\ x10^{-3}\ m^2g^{-1}$ for B1.

$n/c = 1.2333c - 1.705$, $R^2 = 0.9714$ $^1/_{nm}=1.2333$, $nm=0.811\times10^{-3}$ $molg^{-1}$, $^1/_{Knm}=-1.705$, $K=0.7233$, $A=6.0695\ x10^{-3}\ m^2g^{-1}$for B2.

$n/c = 0.1956c + 1.6892$, $R^2 = 0.8451$, $^1/_{nm}=0.1956$, $nm=5.11\times10^{-3}$ $molg^{-1}$, $^1/_{Knm}= 1.6892$, $K=0.1158$ $A=38.2429\ x10^{-3}\ m^2g^{-1}$, for B3.

$n/c = 0.25c + 1.4583$, $R^2 = 0.9643$, $^1/_{nm}=0.25$, $nm=4.0\times10^{-3}$ $molg^{-1}$, $^1/_{Knm}=1.4583$, $K= 0.1714$, $A=29.936\ x10^{-3}\ m^2g^{-1}$, for B4.

The mean were $nm=3.5794\ x10^{-3}\ molg^{-1}$and $K=0.3564$ respectively.

Generally, the surface acidity, n*m* increased as the mass percent of acid used to leach the clay increased proving that the surface area and surface acidity of the clay also increased as a result of the structural changes in the clay lattice.

The linearity of Langmuir adsorption isotherms for the Iliri clays ranged from as low as 0.8451± 0.04 to as high as 0.9997± 0.04. Generally, linearity of Langmuir isotherms increased with increase in mass percent of acid used to leach the clay and temperature of clay activation because surface acidity also increased with increase in concentration of acid and temperature of activation. So the capacity of the clay to bind 1-aminobutane increased and the clay became less able to become saturated with the 1-aminobutane (Hundal, 1988; Nodvin et al, 1986). As the clays could not reach their saturation points easily to invoke competition among the adsorbate molecules, which causes deviation from linearity. When competition sets in, there are steric interactions between the adsorbed and free molecules in solutions (Travis and Etnier, 1981).

For the Iliri clays tested for acidity under different conditions of temperature and concentration of acid used to activate the clays, the slopes of the Langmuir isotherms were positive showing that acidity and surface areas increased with increase in both temperature and concentration of acid used. This observation is in agreement with what was reported by earlier authors (Alemdaroglu et al, 2003; Sarikaya et al, 2000).

The Langmuir adsorption isotherms for Iliri clays were highly linear because the clay acquired a very large surface area on acid leaching on which large number of 1-aminobutane would adsorb without reaching saturation. The quantity of 1-aminobutane adsorbed was a linear function of the equilibrium concentration of 1-aminobutane in the solution. Langmuir equation provides the theoretical adsorption maximum that measures the amine-clay binding energy (Fried and Shapiro, 1956). Beyond a critical concentration value, deviations from linearity occurs showing competition between free amine and adsorbed molecules for the few adsorption sites available in the clay matrices (Olsen and Watanabe, 1957).

The acid-leached clays showed increasing surface acidity with increase in concentration of acid used to leach the clay revealing that surface hydrogens and hydroxyl groups on the silica skeleton had increased. Increase in surface acidity depicted that the interlayer octahedral ions like $Fe^{3+}$, $Fe^{2+}$, $Mn^{2+}$, $Ti^{4+}$ were progressively replaced by hydrogen ions as the concentration of the acid increased. This showed that the Iliri clay was montmorillonite (Bain and Morgan, 1989; Bergaya and Lagaly, 2013).

## CONCLUSIONS

The pH data Iliri clays indicated it was smectite and it developed high acidity on leaching. Basing on acidity, pH, elemental and mineral compositions, the Iliri clay was resolved to contain montmorillonite.

The change in color from grey to white coupled to increase in surface acidity depicted that the interlayer octahedral ions like $Fe^{3+}$, $Fe^{2+}$, $Mn^{2+}$, $Ti^{4+}$ etc were progressively replaced by hydrogen ions as the concentration of the acid increased. This showed that the selected clays conform to structures drawn by earlier authors (Bain and Morgan, 1989; Grim, 1951).

The results on equilibration of 1-aminobutane with slurries of clay powders in hexane indicated that surface acidity and/or general acidity of clays increased with increase in temperature and concentration of acid used in its activation The values of surface acidity, n*m*, for acid-leached Iliri clays ranged from $0.811\text{x}10^{-3}$ $molg^{-1}$ to $6.7705\text{x}10^{-3}$ $molg^{-1}$ and the kinetic equilibrium constant of adsorption, K, varied from 0.07828 to 0.7233 yet the surface area, A increased from 5.2702 $\text{x}10^{-3}$ $m^2g^{-1}$ to 50.6700 $\text{x}10^{-3}$ $m^2g^{-1}$ . The leaching process yielded a very good clay catalyst because the Langmuir isotherms developed using the clays were highly linear.

### Recommendations

The study of adsorption on Iliri clays should be extended to removing inorganic and organic pollutants from waters of Nakivubo Channel.

### Acknowledgement

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