

## STUDIES OF THE EFFECTS OF HYDROCHLORIC ACID-LEACHING ON THE STRUCTURAL AND ADSORPTIVE PERFORMANCE OF NTEJE (NIGERIA) CLAY

By

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### Abstract

The effect of hydrochloric acid-leaching on the structural and adsorptive performance of clay from Nteje was studied in this work. The clay was mined, washed to remove dirt, and sun-dried for two days. The dried clay sample was grinded to a particle size of 0.075 mm. The sized samples were then reacted with different concentrations of hydrochloric acid ranging from 1 – 5M. The structural effects of the acid activation were analyzed by instrumental characterization of the raw and activated samples using Fourier transforms infrared spectroscopy (FTIR) and x-ray fluorescence (XRF). The analyses showed that hydrochloric acid leaching caused an exchange of  $Al^{3+}$ ,  $Fe^{3+}$ , and  $Mg^{2+}$  with  $H^+$  ions which led to the modification of the clay crystalline structure and the surface area of the activated samples was observed to increase to more than four times that of the raw sample. The adsorptive performance of the activated samples was investigated by using the samples to remove colour pigments from palm oil. The results showed that the adsorptive performance of the activated samples was enhanced over that of the raw sample with the sample activated with 3M HCl given the best result. The adsorptive capacity increased from 35.7% (using the raw clay sample) to 88.9% (using the 3M HCl activated sample).

**Keywords:** Characterization; Acid-leaching; Adsorption; Hydrochloric acid; Clay.

### Introduction

Natural clays are acquiring prominence as low-cost adsorbents over the last few decades due to their local and abundant availability and the capability to undergo modification to enhance the surface area, adsorption capacity, and range of applicability (Monvisade and Siriphannon, 2009). The presence of net negative charge on the surface of the clay material, qualifies clays as effective adsorbent for the removal of colour pigments from palm oil and also removal of dyes from solutions. In addition, the adsorption capacity of natural bentonite is hampered by its small surface area and this has led to the need for researches in the fields of clay modifications to enhance their adsorption performance.

Palm oil is a major source of dietary for people in the western part of Africa and this oil has some storage and use difficulties. Palm oil congeals on storage at ambient temperature and has a very low smoke point, which makes it unsuitable for frying. These difficulties can be reduced if the oil can be bleached to remove the impurities. Impurities present in palm oil can be reduced appreciably by adsorption process or bleaching by using clay mineral adsorbents. Clay minerals may be used both naturally and after some chemical or physical treatments such as acid activation, calcination, and ion exchange according to their area of application (Ayari, et al, 2005, 2007). Clay minerals generally show limited adsorbing capacity in their natural state, but they are greatly enhanced by being treated with strong acids at slightly elevated temperature (Foletto et al, 2003; Nguetnkam et al, 2008). When clay minerals are acid activated, initially interlayer cations are replaced with hydrogen ions of the acid with subsequent dissolution of structural cations. The desired changes in the adsorptive properties of clay minerals occurring as a result of acid activation depend considerably on acid leaching conditions (Motlagh, et al, 2011). Several acid activation experiments under different operating conditions have been reported in the literature, in particular the choice of acid concentration, activation time and temperature, and clay to acid ratio (Al-Zahrani, et al, 2000; Bakhtyar et al, 2011; Motlagh, et al, 2008; Diaz and Santos, 2001; Makhoukhi, et al, 2009; Salawudeen, et al, 2007; Zhansheng, et al, 2006; Foletto, et al, 2011; Motlagh et al, 2011; Temuujin, et al, 2006; Woumfo, et al, 2007; Onal, et al, 2002; Temuujin, et al 2004). Activation is the chemical or physical treatment applied to certain types of clays to develop a capacity to absorb colouring matter and other impurities in oils (vegetable, animal, and petroleum). Acid activated clay materials are widely used in various fields, for example, catalysts, catalyst beds, adsorbents, and bleaching earth. The most important applications of the bleaching earth are purification, decolourization, and stabilization of vegetable oils, otherwise, bleaching. They are able to remove undesirable colours by decreasing the levels of chlorophyll, carotene, and other colour bodies, to reduce traces of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , phospholipids, and soaps. Christidis et al, (1997) examined the bleaching capacity and acid activation of bentonite from Aegean, Greece, observing a five-fold increase of the surface area of raw materials. The activated samples were rendered suitable for bleaching of rapeseed oil. It was determined that the optimum bleaching capacity is not associated with maximum surface area and the optimum conditions for activation are obtained by using a variety of combinations of acid strength and residence time. The preparation of acid-activated clay materials must be controlled in order to obtain maximum bleaching capacity (Kiralı and Lacin, 2006; Rozic et al, 2010). Usman et al, (2012) investigated the applicability of clay from Ibeshe in bleaching palm oil. They observed that the clay after acid activation only increased the colour reduction from 9.1 % to 27.3%, a poor performance as an adsorbent. Motlagh et al, (2011) reported that acid activation of clay from Khorasan, Iran, increased its adsorbing ability from 6.35% to 96.4% efficiency using 5N sulphuric acid.

This work was carried out in order to study the structural effects on Nteje natural clay after acid-leaching with hydrochloric acid by characterizing the natural and acid-leached clay samples and also verify the adsorptive performance of the acid-leached clay in bleaching palm oil.

## Materials and Methods

### Materials

Ash-coloured clay material from Nteje (N: 6° 16' 00"; E: 6° 55' 00"; A: 118m) in Aniocha local government area of Anambra state, Nigeria was used as the primary raw material. Refined palm oil was obtained at oil mill located at Isuofia (N: 6° 1' 60"; E: 7° 2' 60"; A: 361m). All chemicals used were analytical grade, bought from Conraws Company Ltd, Enugu.

### Experimental Methods

#### Acid activation of the clay sample

The clay material was prepared for activation by air-drying and grinding to a particle size of 0.212 mm. 10 g of the prepared sample was weighed into flask (250ml capacity) and 100 ml of hydrochloric acid solution was added. The resulting suspension was heated on a magnetically stirred hot plate at temperature of 90 °C for 2 hours 30 minutes. At the end of the experimental duration, the resulting slurry was poured into a Buchner funnel to separate the acid and clay. The residual clay was washed severally with distilled water until neutral point was obtained with pH indicator. The clay residue was dried in an oven at 80 °C for 4 hours. The dried samples were crushed and sieved again to 0.212 mm particle size. The activation process was repeated with varying acid concentrations of 1 – 5M of HCl, varying time of 30 – 150 minutes, and varying temperatures of 70 – 120 °C. The clay samples thus prepared were labeled NT0, NT1, NT2, NT3, NT4, and NT5, where the numbers indicate the acid concentrations used in the activation step.

#### Characterization

The chemical and mineralogical compositions of the natural and activated clay samples were determined. The chemical composition was determined using X-ray fluorescence (XRF), Philips PW 2400 XRF spectrometer; while the mineralogical composition was determined using Fourier transform infrared (FTIR), Shimadzu S8400 spectrophotometer, with samples prepared by the conventional KBr disc method. The specific surface area was measured at 77K by BET method with a Micromeritics Gemini 2360 instrument using N<sub>2</sub> gas.

#### Adsorption experiment

The adsorption/bleaching experiments were carried out in a batch process. 50 g of the refined palm oil were charged into a 250 ml beaker and 2 g of the activated clay samples were also added. The mixture of clay and oil were heated placed in a water bath and heated to a temperature of 80 °C for 30 minutes under continuous stirring. At the end of the reaction, the slurry formed was filtered through a dry filter paper. The bleaching capacity of the acid activated clays was then determined by measuring the colour of the bleached oils using a UV-Vis spectrophotometer (Shimadzu UV mini 1240) at wavelength of 450 nm. The bleaching efficiency of the acid activated clay was calculated in this study using the following equation:

$$\% \text{ bleaching efficiency} = [A_{\text{unbleached}} - A_{\text{bleached}} / A_{\text{unbleached}}] \times 100 \quad (1)$$

Where  $A_{\text{unbleached}}$  and  $A_{\text{bleached}}$  are the absorbencies of the unbleached and bleached oils, respectively.

## Results and Discussions

### Characterization

The results of the x-ray fluorescence analysis of the raw and activated clay samples are shown in Table 1. The table shows a decrease in the chemical composition of the acid-leached clay samples as the acid concentration increases and a corresponding increase in the surface area and adsorption efficiency. As can be seen in the table, the  $\text{Si}^{4+}$  cations are not removed, but increased with increase in acid treatment, this could be as a result of depletion of the cations from the interlayer and octahedral sheets of the clay (Motlagh et al, 2011). More of the exchangeable cations were easily removed under mild treatment with the acid; such cations include  $\text{Ca}^{2+}$  and  $\text{K}^+$ . Their dissolution remained almost constant after treating with 4M acid concentration. The dissolution of the octahedral cations ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mg}^{2+}$ ) was continuous as the acid concentration increased.

As the acid activation is increased, the surface area increased rapidly and reached a maximum and dropped. The increase in surface area is attributed to the removal of impurities, replacement of exchangeable cations ( $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$ ) with hydrogen ions and leaching of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mg}^{2+}$  from the octahedral and tetrahedral sites which exposes the edges of the clay particles (Tsai et al, 2007). Further increase in the acid concentration beyond 4M of HCl showed a decrease in the surface area as shown in Figure 1. The decrease in surface area at higher acid concentrations is attributed to the deeper penetration of the acid into the voids and excessive leaching of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mg}^{2+}$ , resulting in the collapse of the layered crystalline structure of the clay material (Korichi et al, 2009).

Table 1: Chemical analysis, specific surface area, maximum bleaching efficiency and cation exchange capacity (CEC) of the natural and acid activated Ukpork clay samples

Chemical composition (%)	Clay sample					
	NT0	NT1	NT2	NT3	NT4	NT5
$\text{Al}_2\text{O}_3$	21.70	15.64	12.48	9.87	7.23	6.85
$\text{SiO}_2$	45.80	54.72	58.62	64.25	66.34	67.21
$\text{Fe}_2\text{O}_3$	17.46	12.86	10.54	8.08	7.16	6.81
$\text{CaO}$	0.22	0.09	0.07	0.06	0.05	0.05
$\text{MgO}$	4.78	2.23	1.87	1.23	0.98	0.85
$\text{K}_2\text{O}$	1.90	0.98	0.72	0.65	0.61	0.60
$\text{TiO}$	2.40	1.14	1.08	0.84	0.53	0.44
$\text{MnO}$	0.03	0.02	0.01	0.01	0.01	0.01
$\text{CuO}$	0.13	0.08	0.07	0.06	0.05	0.05
$\text{ZnO}$	0.04	0.02	0.01	0.01	0.01	0.01
LOI	5.54	2.38	2.04	1.87	1.46	1.09
$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	97.6	195.9	245.8	316.8	352.4	334.2
Max. Bleaching efficiency (%)	35.7	47.4	58.9	88.9	73.6	68.4
$\text{Si}/(\text{Al} + \text{Fe} + \text{Mg})$	0.93	1.50	2.01	2.52	2.90	3.37
Cation exchange capacity (CEC), meg/100g	98	76	63	54	50	49

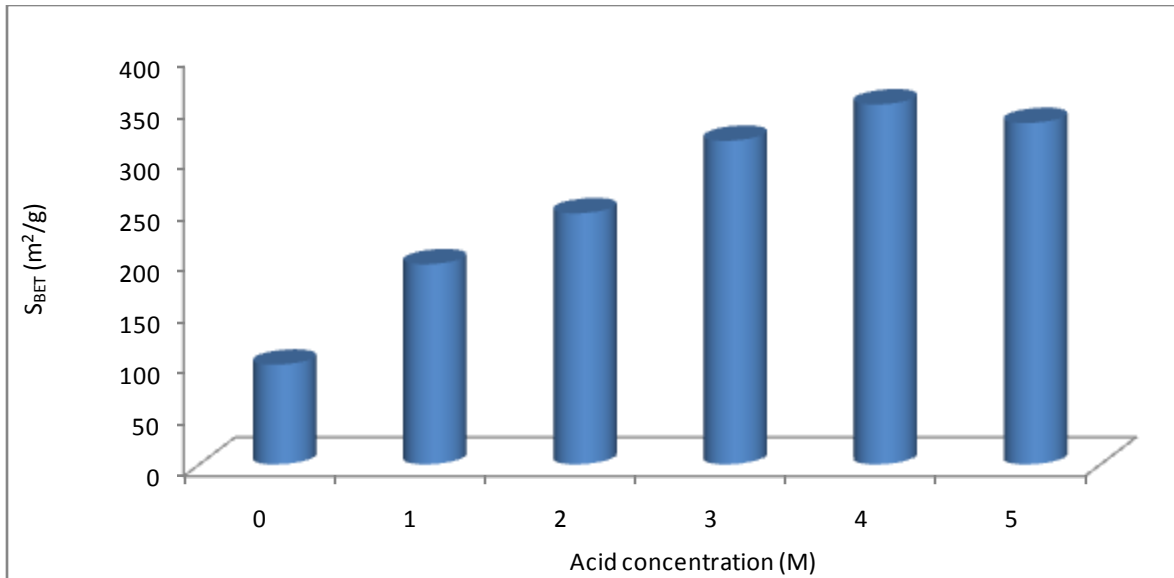


Figure 1: Specific surface area ( $S_{BET}$ ) of clay samples modified by acid activation with different concentrations of HCl.

#### Fourier transforms infrared spectroscopy (FTIR) analysis

The FTIR spectra of the raw and acid-leached clay samples were carried out in the range from 400 – 4000  $cm^{-1}$  to study the effect of acid-leaching on the clay mineral. The FTIR spectra of the raw and acid-leached samples are shown in Figures 2 and 3, respectively. The changes in the functional groups provide the indication of the modifications that occurred during the activation process. During the acid-leaching of the clay samples the protons from the acid medium penetrate into the clay structures attacking the OH groups thereby causing the alteration in the adsorption bands attributed to the OH vibrations and octahedral cations. The intensities of the stretching bands observed at 3623, 3432, 1641, and 920  $cm^{-1}$  (associated with O-H, along with Al-OH stretch) decreased after acid-activation. The increase in the severity of acid caused the disappearance of the stretching bands at 4660, 3694, 2376, and 998  $cm^{-1}$  assigned to the H-O-H stretching. The peak assigned to Si-O-Si stretch at 788 and 1066  $cm^{-1}$  remained after acid leaching, similar result was reported by others (Christidis et al, 1997; Komandel et al, 1990). The bands at 525, 690, and 998  $cm^{-1}$  disappeared after the acid treatment of the clay sample. The transformation of the tetrahedral occurred at 788  $cm^{-1}$  which was increased after the acid treatment. Positions and assignment of the vibrational bands of the raw and acid-leached clay samples are shown in Table 2.

Table 2: Wave numbers and assignment of the bands in the IR spectra of the untreated and 3M of HCl treated samples.

Transmittance ( $cm^{-1}$ )		Assignment
NT0	NT3	
525	-	Al-O-Si/ Fe-O bending
565	560	Si-O bending
690	-	Al-OH bending
788	789	Si-O-Si/ Si-O stretching

920	919	Al-O-H stretching
998	-	O-H-O stretching
1066	1038	Si-O-Si stretching
1641	1654	Si-O-Si bending
2376	-	H-O-H bending
3432	3415	O-H bending
-	3553	Si-O-Al bending
3623	3620	O-H stretching
3694	-	O-H stretching
4660	-	H-O-H stretching

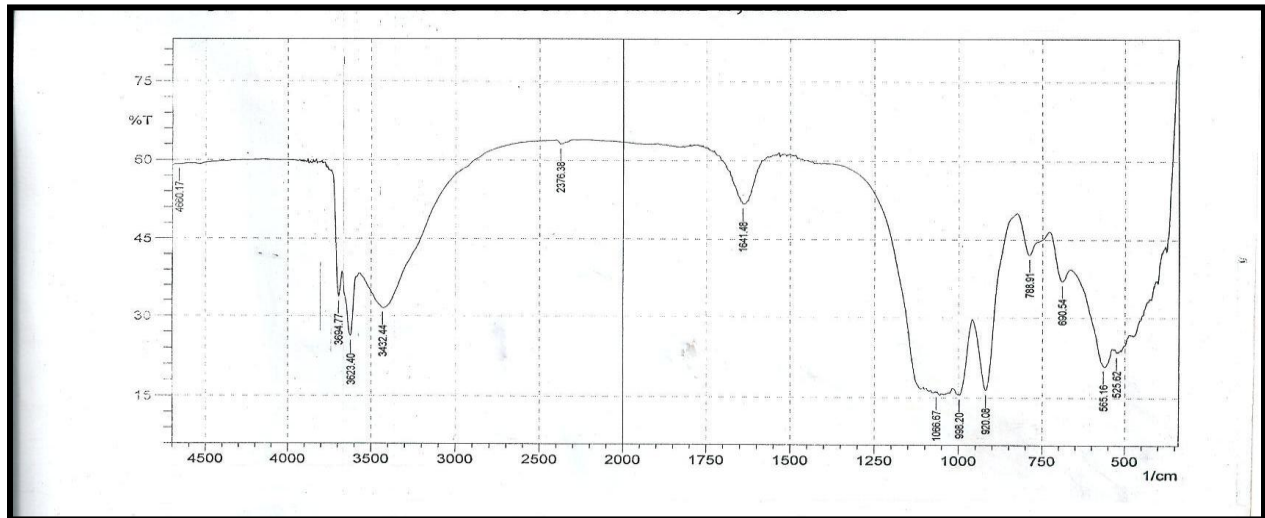


Figure 2: FT-IR spectra of natural Nteje clay.

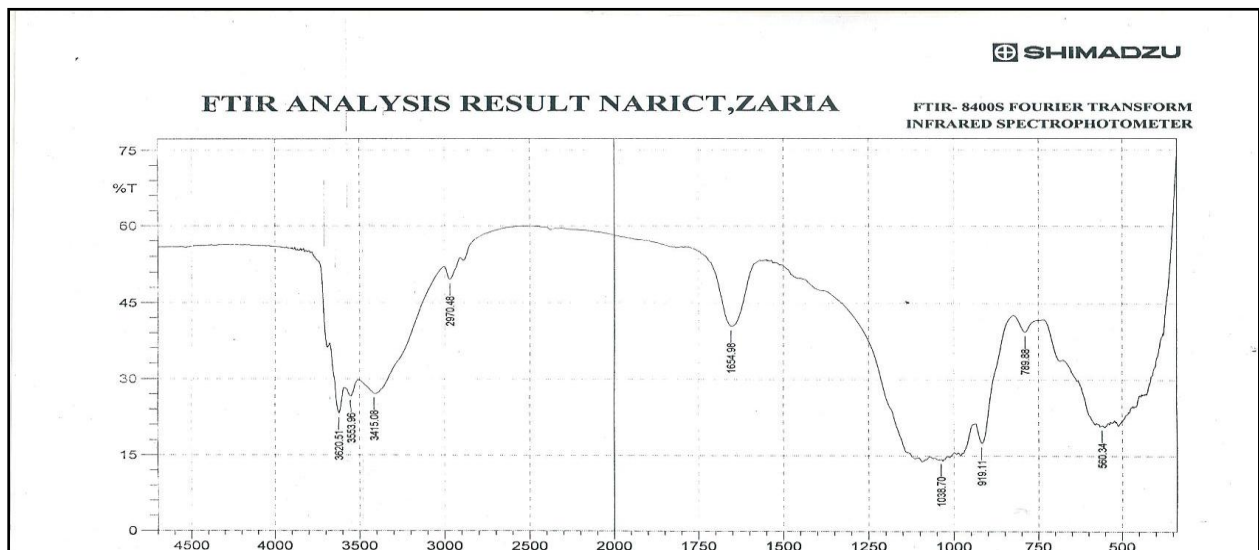


Figure 3: FT-IR spectra of acid-activated Nteje clay.

The specific surface area of any clay sample plays very important role in the physical and chemical properties of the samples. It is clear from Table 2 that the surface area of the acid-leached clay samples increased by increasing the acid concentration. This increase in surface area is as a result of the leaching of the octahedral cations from the inter layer of the samples, and this shows a relationship between the surface area and the amount of  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{MgO}$  in the samples. Figure 4 shows that at higher amount of these oxides, the sample depicts low surface area. Thus, the surface area of the activated samples increases as the amount of  $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{MgO})$  content decreases.

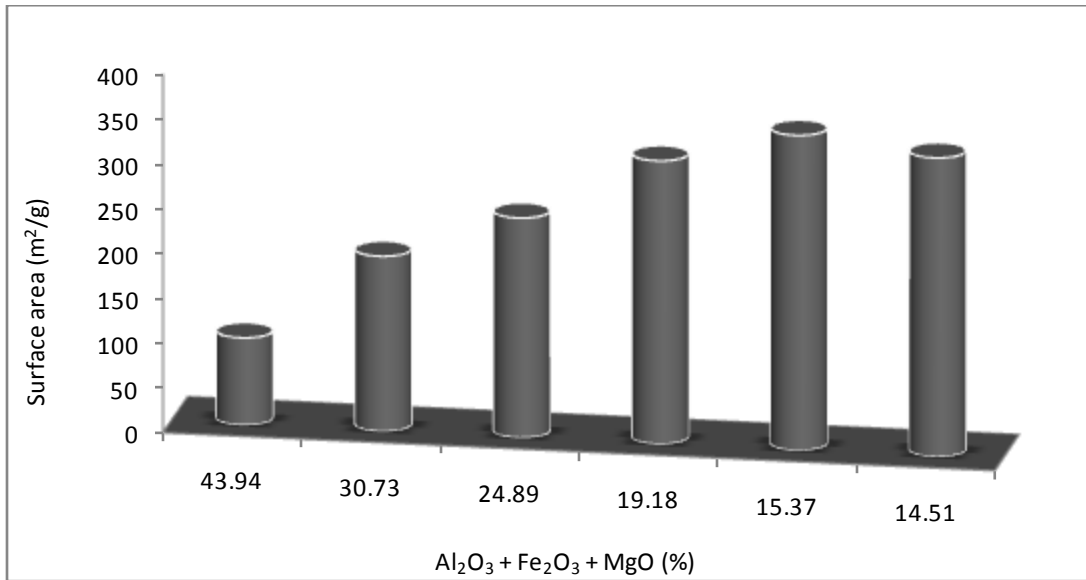


Figure 4: The variation of surface area by the % content of  $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{MgO})$ .

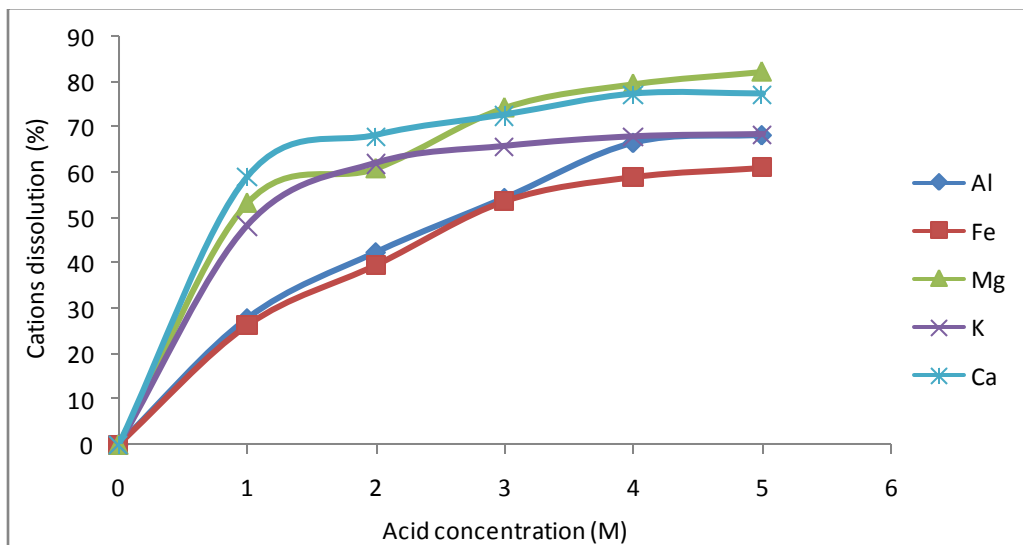


Figure 5: Effect of acid concentration on the removal of the octahedral cations.

Figure 5 shows the dissolution of the cations from the clay layer as the acid concentration increased. From the figure it is clear that the cations  $\text{Ca}^{2+}$  and  $\text{K}^{+}$  are easily removed at lower acid concentration, while the cations  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mg}^{2+}$  are removed appreciably at higher acid concentration.

### Bleaching efficiency

The results of the bleaching studies performed using the natural and acid-leached samples are shown in Figure 5. The figure shows that the bleaching efficiency increases with an increase in the acid concentration used in the activation step. From the figure, the sample activated with 3M hydrochloric acid gave the most bleaching efficiency. The maximum bleaching efficiency does not correspond to the maximum surface area value. As can be observed from Table 1 and Figure 5, NT4 has a surface area of  $352.4\text{m}^2/\text{g}$  and a maximum bleaching efficiency of 73.6%, while NT3 has a surface area of  $316.8\text{m}^2/\text{g}$  with a maximum bleaching efficiency of 88.9%. Naturally, NT4 should be expected to have higher bleaching efficiency as a result of higher surface area value. It has been reported by researchers (Inglethorpe, et al, 1993; Diaz et al, 2001; Engelhard, 1996) that the optimum decolourizing ability of activated clay (for a given set of activating conditions) may or may not coincide with its maximum value of the surface area attained under those conditions.

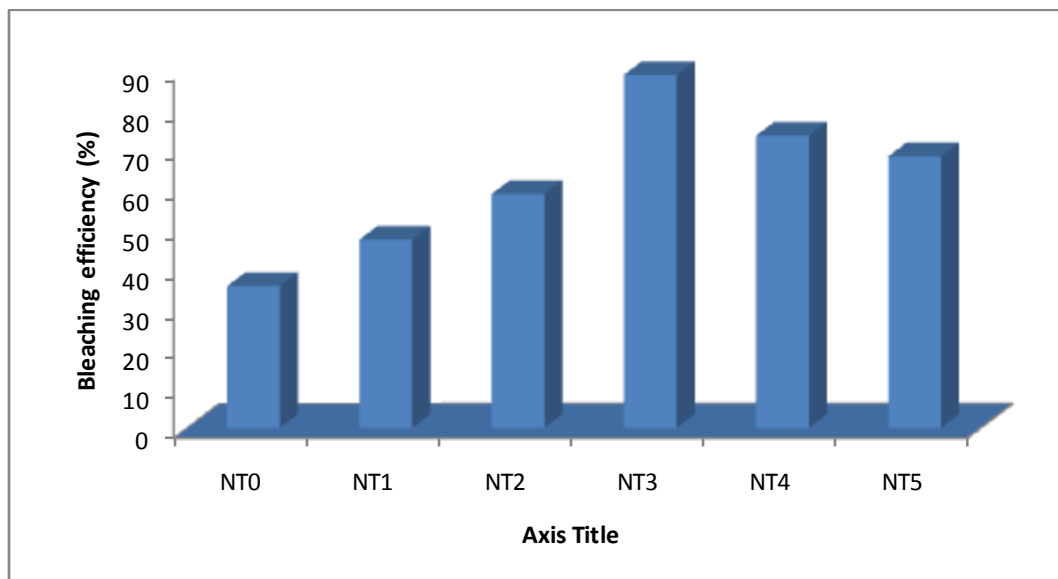


Figure 6: Bleaching efficiency of the raw and activated clay samples.

### Conclusion

The effect of hydrochloric acid-leaching on the structural properties and bleaching performance of Nteje clay has been successfully investigated. The structure of the clay was modified by the acid-leaching process and the bleaching efficiency was increased from 35.7 to 88.9%. Based on the results activated



clay from Nteje performs better than the un-activated one and the acid concentration play an important role in the activation step.

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