Enhancement Of Physicochemical Properties Of Nteje Clay To Increase Its Bleaching Performance Using Acid Activation

R. O. Ajemba

Department of Chemical Engineering, Nnamdi Azikiwe University, P. M. B. 5025, Awka, Anambra, Nigeria

ABSTRACT

This study was aimed at analyzing the physicochemical properties of clay mineral from Nteje after sulphuric acid activation. The clay was grinded to a particle size of 0.212 mm and reacted with different concentrations of sulphuric acid ranging from 2 – 7 mol/L. The untreated and treated samples were characterized. The adsorptive capacities of the samples were investigated by using them to bleach palm oil. Results of the characterization showed that acid activation modified the chemical composition of the clay mineral. The analyses showed that acid activation caused an exchange of the octahedral cations; Al^{3+}, Fe^{3+}, and Mg^{2+} with H^+ ions which led to the modification of the clay crystalline structure and the surface areas of the modified samples were observed to increase to more than three times that of the raw sample. The adsorption results showed that the adsorptive performance of the modified samples was improved over that of the raw sample. The adsorptive capacity increased from 43.4% to 92.5% (using the 6 mol/L of H_2SO_4 activated sample). The equilibrium result showed that the adsorption occurred in multi-layer in agreement with Freundlich adsorption isotherm model. This study has shown that the physicochemical properties of Nteje clay were enhanced by acid activation thereby making the clay an effective adsorbent for palm oil bleaching.

Keywords: activation, adsorption, bleaching, colour pigment, palm oil, surface area.

1. INTRODUCTION

Clay minerals, enormously abundant in nature, have been considered as a potential source of adsorbent for removing colour pigments from edible oils. Nonetheless, the effective application of these materials in this area is limited due to small surface area and presence of net negative surface charge, leading to low adsorption capacity. All these factors have led to the need for research and development in the field of modification of clay surfaces to enhance their adsorptive properties. Surface modified clays have high potential to provide an alternative to most widely used activated carbon. Therefore, in order to ameliorate the adsorption properties and range of applicability, a number of physical and chemical methods have been investigated to modify the clays, including heat treatment [1, 2], acid activation [3-8], treating the cationic surfactants [9], and polymer modification [10, 11]. Nigeria is endowed with vast deposits of clay minerals that are unharnessed. The deposit located at Nteje has not been employed industrially, but, it is only used for local pottery work by the rural inhabitants. Palm oil is a major source of dietary food 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.   Christidis et al, [12] 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 [13, 14]. Usman et al, [15] 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.

2. MATERIALS AND METHODS

2.1. Materials

Ash-coloured clay material from Nteje (N: 5° 54' 27.5"; E: 6° 56' 3.7"; A: 137m) 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.

2.2.   Experimental Methods

R. O. Ajemba / International Journal of Engineering Research and Applications
(IJERA)   ISSN: 2248-9622   www.ijera.com
Vol. 2, Issue 4, July-August 2012, pp.281-288

2.2.1.   Acid activation of the clay sample

The clay material was prepared for activation by air-drying and grinding to a particle size of 0.075 mm. 10 g of the prepared sample was weighed into flask (250ml capacity) and 100 ml of sulphuric acid solution was added. The resulting suspension was heated on a magnetically stirred hot plate at temperature of 90 ^{0}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 ^{0}C for 4 hours. The dried samples were crushed and sieved again to 0.075 mm particle size. The activation process was repeated with varying acid concentrations of 2 – 7 mol/L of H_2SO_4, varying time of 30 – 150 minutes, and varying temperatures of 70 – 120 ^{0}C. The clay samples thus prepared were labeled NT0, NT2, NT3, NT4, NT5, NT6, and NT7, where the numbers indicate the acid concentrations used in the activation step.

2.2.2.   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.

2.2.3.   Surface area determination

The surface area was determined using ethylene glycol mono-ethyl-ether (EGME) described by Carter et al, [16, 17]. Clay samples were sun-dried and grinded to pass No. 40 sieve. A small amount of the sample was then placed in an oven at a temperature of 105 ^{0}C overnight to remove water and then dried with P_2O_5. One gram of the dried sample was spread into the bottom of aluminium tare and weighed (W_a) using an analytical balance with an accuracy of 0.001 g. Approximately 3.0 ml of laboratory grade EGME was added to the sample using a pipette and mixed together with a gentle swirling motion to create uniform slurry. All clay samples were covered with the EGME in order to obtain an accurate surface area measurement. The aluminium tare was then placed inside a standard laboratory glass sealed vacuum desiccator and allowed to equilibrate for 20 min. The desiccator was then evacuated using vacuum pump. The aluminium tare was removed from the desiccator and weighed (W_s) after a period of 12, 16, and 24 hours. When the mass of the sample varied by more than 0.001 grams between two measurements, the sample was placed back in the desiccator and evacuated again for an additional 2 hours. The process was continued until the sample mass did not vary by more than 0.001 g. The surface area was expressed as follows:

$$A = \frac{W_a}{0.000286\,W_s}$$

(1)

A = surface area, W_a = weight of EGME retained by the sample, W_s = weight of P_2O_5-dried sample, 0.000286 is the weight of EGME required to form uni-molecular layer on a square meter of the surface [18].

2.2.4.   Bleaching experiment

The 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 placed in a water bath and heated to a temperature of 80 ^{0}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:

$$\% \, Bleaching \, Efficiency = \frac{[A_{unbleached} - A_{bleached}]}{A_{unbleached}} \, x \, 100$$

(2)

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

3.   RESULTS AND DISCUSSIONS

3.1.   Characterization

The changes in the chemical composition of the natural and acid activated Nteje clay at different acid concentrations are shown in Table 1. The content of SiO_2 was observed to increase as the acid concentration increased up to 6mol/L and decreased with further increase in concentration (Fig. 1) and this could be due to the formation of mullite which protects the clay layers from further acid attack. The contents of the octahedral cations (Al_2O_3, Fe_2O_3, and MgO) decreased intensely as the acid concentration increased and increased with further attack after 6 mol/L concentration (Fig. 2). The behaviour showed by the Al_2O_3, Fe_2O_3, and MgO contents with progressive acid treatment is related to the progressive dissolution of the clay mineral. The octahedral sheet destruction passes the cations into the solution, while the silica generated by the tetrahedral sheet remains in the solid phase due to its insolubility [19]. Pesquera et al [20] suggest that this free silica generated by the initial destruction of the tetrahedral sheet, is polymerized by the effect of such high acid concentrations and is deposited on the undestroyed silicate fractions, thereby protecting it from further acid attack.

Table 1: Chemical analysis, specific surface area, and maximum bleaching efficiency of the natural and acid activated Nteje clay samples determined by XRF

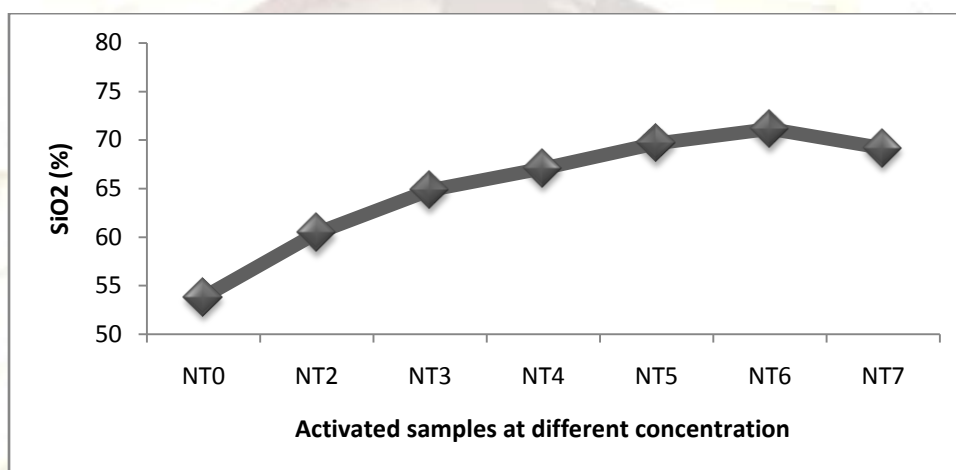| Chemical composition (%)	Clay samples						
	NT0	NT2	NT3	NT4	NT5	NT6	NT7
Al_2O_3	19.45	14.85	11.54	9.86	7.64	6.06	6.74
SiO_2	53.82	60.43	64.83	67.07	69.63	71.14	69.15
Fe_2O_3	16.58	10.71	7.26	5.93	4.06	2.15	2.63
CaO	1.50	1.22	0.99	0.78	0.63	0.49	0.47
MgO	1.78	1.36	0.97	0.75	0.57	0.41	0.40
K_2O	0.90	0.57	0.38	0.17	0.11	0.09	0.08
LOI	5.97	2.98	1.99	1.54	1.21	0.97	0.87
Surface area (m^2/g)	87	176	215	234	258	286	269
Si/(Al + Fe + Mg)	1.42	2.24	3.28	4.06	5.67	8.25	7.08

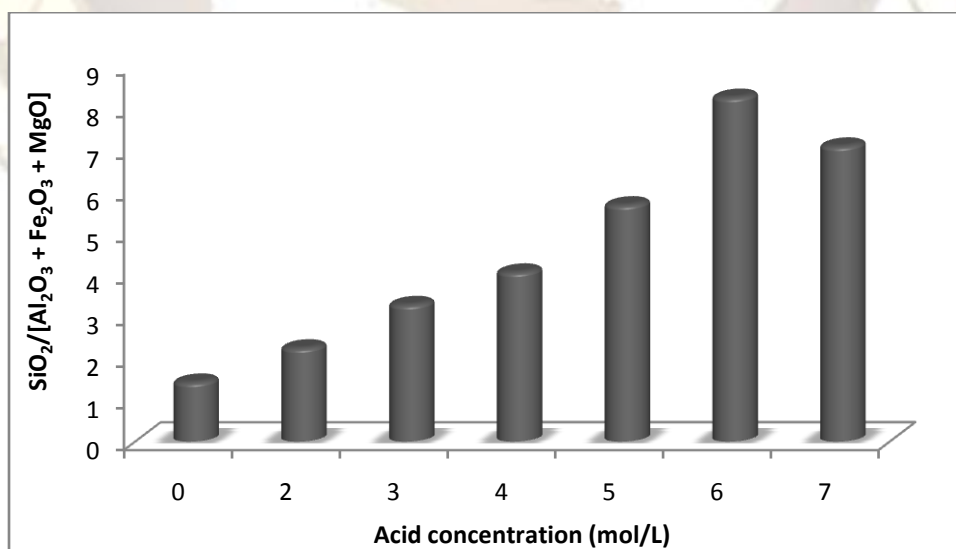Figure 1: SiO_2 content of the clay sample after activation with H_2SO_4.

Figure 2: Variation of SiO_2 / [Al_2O_3 + Fe_2O_3 + MgO] ratios with acid concentration.

It was observed from the surface area analysis of the natural and treated samples that the surface area increased as the acid concentration used in the activation step increased. The increase in surface area from natural to activated samples is related to the elimination of the exchangeable cations, de-lamination, and the generation of micro-porosity during the processes [19]. This increase continued up

to the sample activated with 6 mol/L of H_2SO_4 and dropped when the concentration was increased to 7mol/L (Fig. 3). This is attributed to the polymerization of the generated free silica by the effect of excess acid concentration and is deposited on the surface of the clay particle preventing it from further attack [20].
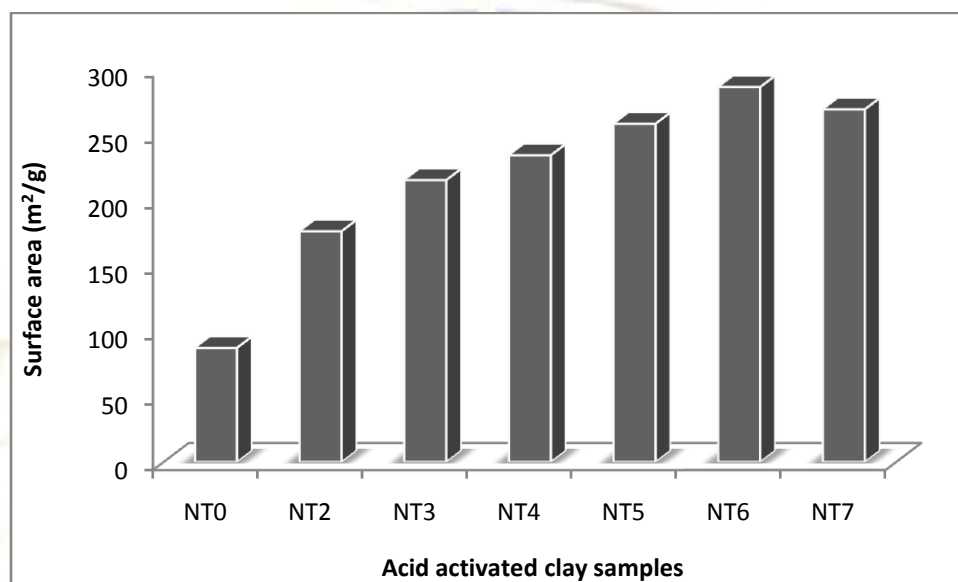

Figure 3: Variation of the surface area with acid concentration treatment of the samples.

3.2. Fourier transforms infrared (FTIR) spectroscopy 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 Figs 4 and 5, 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 [12, 21]. 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.
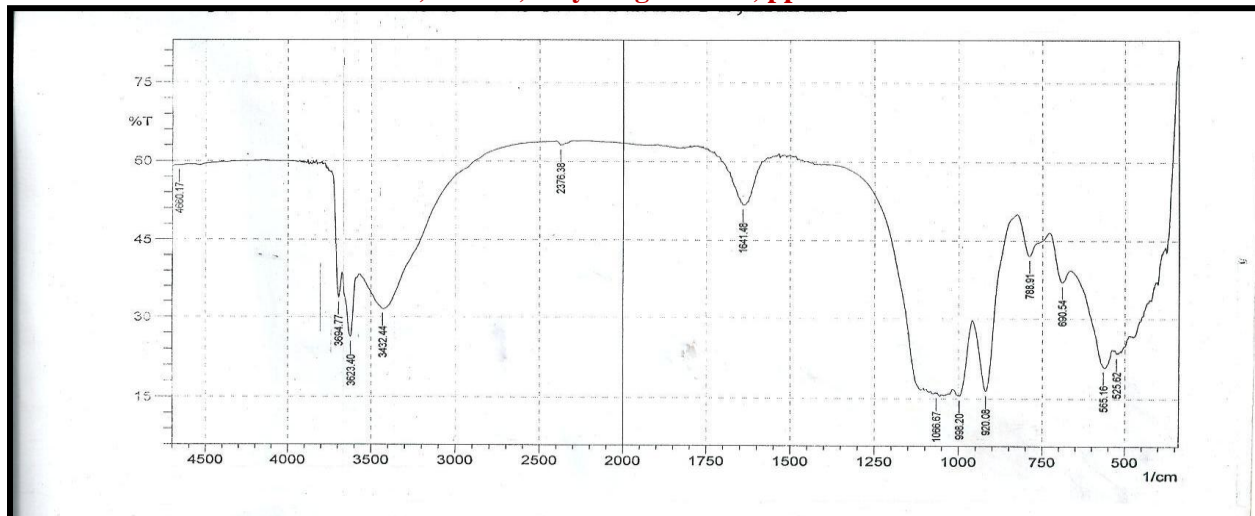
R. O. Ajemba / International Journal of Engineering Research and Applications
(IJERA)   ISSN: 2248-9622   www.ijera.com
Vol. 2, Issue 4, July-August 2012, pp.281-288

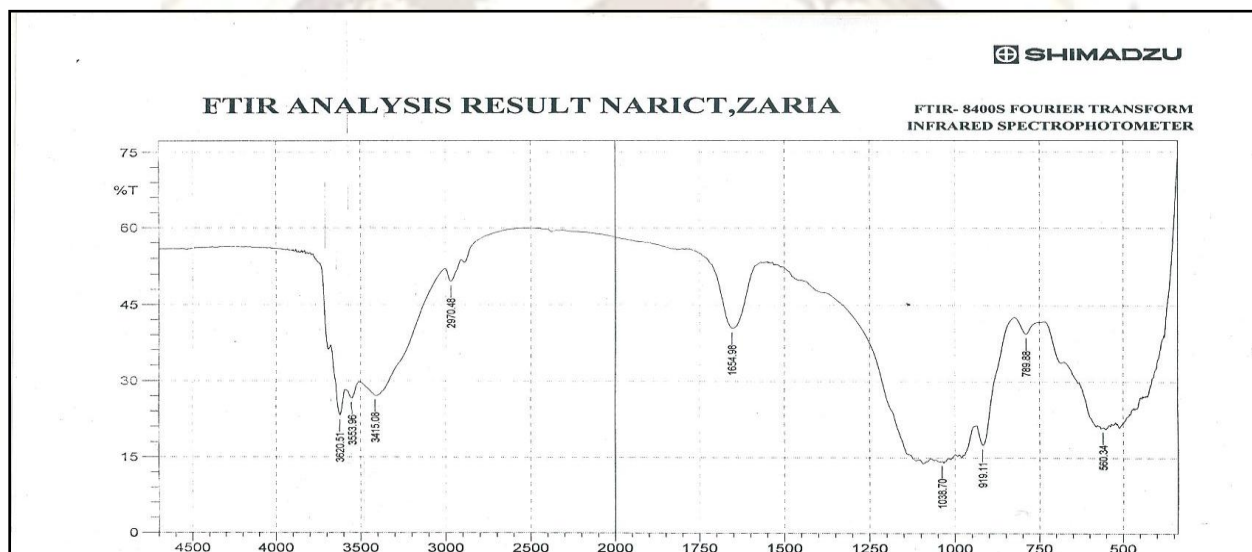Figure 4: FT-IR spectra of natural Nteje clay.

Figure 5: FT-IR spectra of acid-activated Nteje clay.

3.3. Bleaching Studies

The results of the bleaching studies performed using the natural and acid activated samples are shown in Fig. 6. The figure shows that the bleaching efficiency increases with increase in the acid concentration used in the activation step. The increase reached a maximum with the sample activated with 6mol/L H_2SO_4 and decreased thereafter with further increase in the acid concentration. This decrease in bleaching efficiency is attributed to the small surface area and Si / [Al_2O_3 + Fe_2O_3 + MgO] ratio exhibited by the sample activated with 7mol/L of H_2SO_4 that led to the destruction of the clay crystalline structure as shown in Fig. 7.
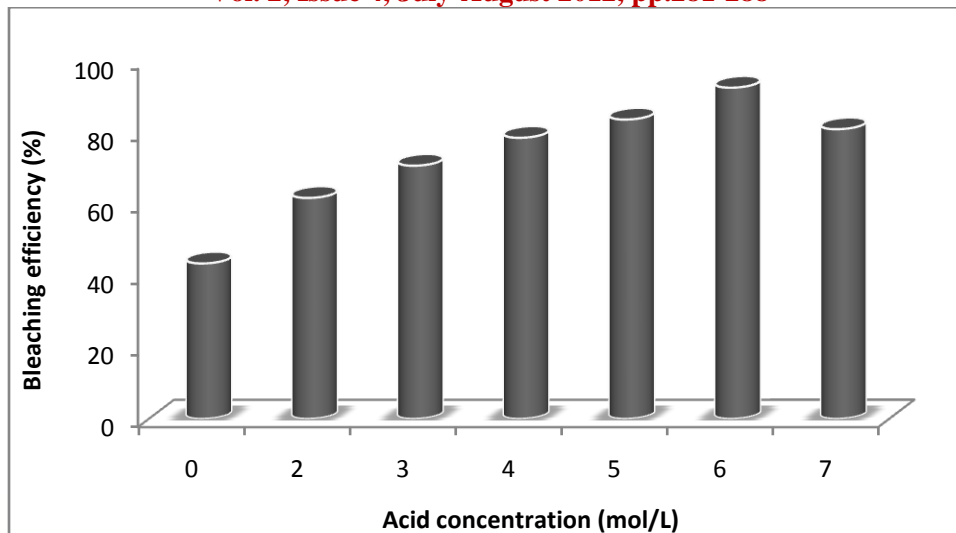
Figure 6: Variation of the bleaching efficiency with acid concentrations used in the activation
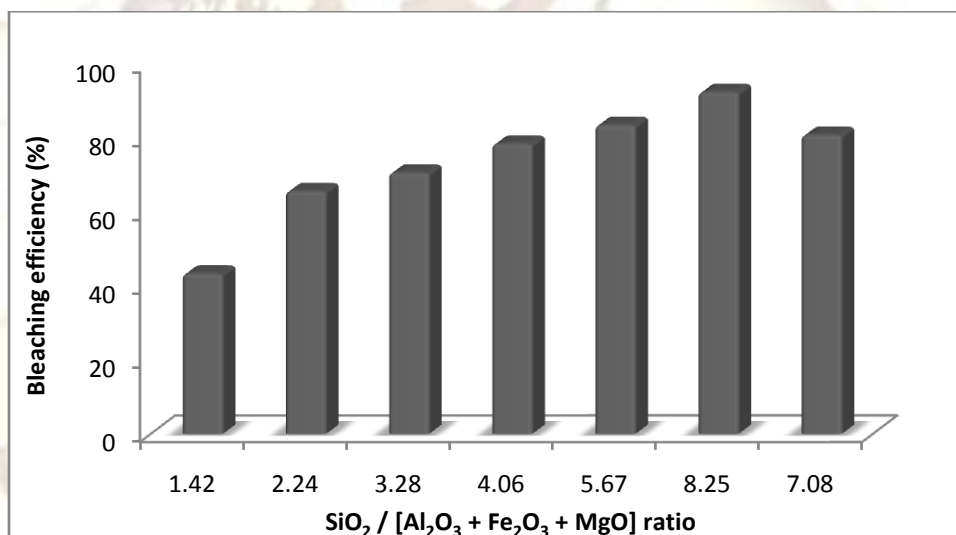

Figure 7: Variation of the bleaching efficiency with $SiO_2 / [Al_2O_3 + Fe_2O_3 + MgO]$ ratio.

3.4. Adsorption Isotherms

The mechanism of adsorption of the colour pigments onto the acid modified Udi clay was determined by evaluating the equilibrium data obtained from the experiments. In this study, both the Langmuir and Freundlich isotherm models were used to analyze the adsorption experimental data. The basic assumption of Langmuir model is that the formation of monolayer takes place on the surface of the adsorbent indicating that only one colour pigment molecule could be adsorbed on one adsorption site and the intermolecular forces decrease with the distance. The model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$
(3)

Where C_e is the equilibrium concentration of the pigments (mg/l), q_e is the amount of colour pigment adsorbed per unit of adsorbent (mg), q_m the Langmuir constant for adsorption capacity (mg/g) and K_L is the Langmuir constant for energy of adsorption (L/g). The values of q_m and K_L were obtained from the slopes and intercept of the linear plots of C_e/q_e versus C_e (not shown) and are shown in Table 2.

The Freundlich model is applicable to heterogeneous systems and it involves the formation of multi-layers. The Freundlich adsorption isotherm is given by the equation:

R. O. Ajemba / International Journal of Engineering Research and Applications
(IJERA)   ISSN: 2248-9622   www.ijera.com
Vol. 2, Issue 4, July-August 2012, pp.281-288

$$\log q_e = \log k_f + \frac{1}{n}(\log C_e)$$
(4)

Where k_f and n are the Freundlich constants and represent the adsorption capacity and measure of heterogeneity, respectively. The values of k_f and n were obtained from the slopes and intercepts of the linear plots of q_e versus C_e as shown in Fig. 8 and the values

are presented also in Table 2. A comparison of the values of the coefficient of determination (R^2) shown in Table 2, shows that the adsorption experimental data conformed better to the Freundlich adsorption isotherm and therefore, it can be concluded that the adsorption of colour pigments onto acid modified Nteje clay occurred in   multi-layer.
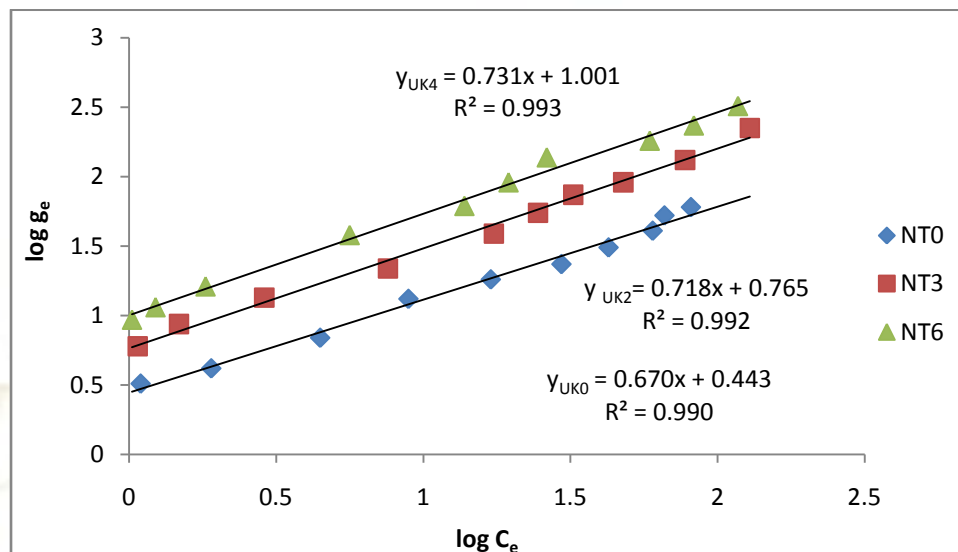

Figure 2: Freundlich adsorption isotherm for colour pigment adsorption onto acid modified Nteje clay.

Table 2: Freundlich and Langmuir isotherm constants and the respective correlation coefficients

Isotherm Model	Model Parameters	Clay Type		
		UD0	UD300	UD8
Langmuir	q_m	72.43	74.61	83.75
	K_L	0.074	0.072	0.083
	R^2	0.986	0.982	0.988
Freundlich	k_f	2.77	5.82	10.02
	n	1.49	1.39	1.37
	R^2	0.990	0.992	0.993

4. CONCLUSIONS

The physicochemical properties of Nteje clay by sulphuric acid activation have been successfully investigated. Results of this work show that acid concentration highly affects the physicochemical properties. The structural change obtained by FTIR analysis indicates that the destruction of the octahedral sheet is a function of acid concentration. The acid activation increased the surface area to more than three times the area of the untreated sample. The acid activated Nteje clay yielded an adsorbent material that is efficient in bleaching off colour pigments from palm oil more than the untreated samples. The equilibrium result shows that the adsorption of colour pigment onto the treated and

untreated clay samples occurs in multi-layers in agreement with the Freundlich adsorption model. The results of this work have shown that the physicochemical properties of Nteje clay are enhanced by sulphuric acid activation thereby making the clay a good source of adsorbent for the bleaching of palm oil. This study only analyzed the samples using FTIR due to the unavailability of other equipments such as X-ray diffractometer

REFERENCES

[1] Al-Asheh S., Banat F., Abu-Aitah L., Adsorption of phenol using different types of activated bentonites. *Separation Purification Technology, 33,* 2003, 1 – 10.

[2] Chaisena A., Rangsriwatananon K., Effects of thermal and acid treatments on some Physico-chemical properties of Lampang diatomite. *Suranere Journal of Science and Technology, 11 (4),* 2004, 289 – 299.

[3] Zorica P. T., Mladenovic S. B., Babic B. M., Logar V. A., Dordevic A. R., Cupac S. B., Modification of smectite structure by sulphuric acid and characteristics of the modified smectite. *Journal of Agricultural Science, 56 (1),* 2011, 25 – 35.

[4] Motlagh M. M. K., Z. Rigi Z. A., Yuzbashi A. A., To evaluate an acid activated bentonite from Khorasan (Iran) for use as bleaching clay. *International Journal of Engineering Science, 19 (5-2),* 2008, 83 – 87.

[5] Motlagh M. M. K., Youzbashi A. A., Rigi Z. A., Effect of acid activation on structural and bleaching properties of a bentonite. *Iranian Journal of Material Science & Engineering, 8 (4),* 2011, 50 – 56.

[6] Taha K. K., Tagelsir M. S., Musa A. M., Performance of Sudanese activated bentonite in bleaching cotton seed oil. *Journal of Bangladesh Chemical Society, 24 (2),* 2011, 191 – 201.

[7] Eze K. A., Nwadiogbu J. O., Nwamkwere E. T., Effect of acid treatment on the physicochemical properties of kaolin clay. *Archives of Applied Science Research, 4 (2),* 2012, 792 – 794.

[8] Foletto, E. L., Colazzo G. C., Volzone C., Porto L. M., Sunflower oil bleaching by adsorption onto acid-activated bentonite, Brazilian *Journal of Chemical Engineering, 28 (1),* 2011, 169 – 174.

[9] Wang L., Wang A., Adsorption properties of congo red from aqueous solution onto surfactant-modified montmorillonite. *Journal of Hazardous Materials, 160,* 2008, 173 – 180.

[10] Chen R., Peng F., Su S., Synthesis and characterization of novel swelling tunable oligomeric poly (styrene-co-acrylamide) modified clays. *Journal of Applied Polymer Science, 108,* 2008, 2712 – 2717.

[11] Liu P., Polymer modified clay minerals: A review, *Applied Clay Science, 38,* 2007, 64 – 76.

[12] Christidis G. E., Scott P. W., Dumham A. C., Acid activation and bleaching capacity of bentonites from the islands of Milos and Chios, Aegean and Greece. *Applied Clay Science, 12,* 1997, 329 – 347.

[13] Kirali, E. G., Lacin, O., Statistical modeling of acid activation on cotton oil bleaching by Turkish bentonite, *Journal of Food Engineering, 75,* 2006, 137 – 141.

[14] Rozic L., Novkovic T., Petrovic S., Modeling and optimization process parameters of acid activation of bentonite by response surface methodology. *Applied Clay Science, 48,* 2010, 154 – 158.

[15] Usman M. A., Ekwueme V. I., Alaje T. O., Mohammed A. O., Characterization, acid activation, and bleaching performance of Ibeshe clay, Lagos, Nigeria. *ISRN Ceramics,* 2012, doi:10.5402/2012/658508.

[16] Carter D. L., Heilman M. D., Gonzalez C. L., Ethylene Glycol Mono-ethyl Ether for determining surface area of silicate minerals, *Soil Science, 100(5),* 1965, 356 – 360.

[17] Carter D. L., Mortland M. M., Kemper W. D., Specific surface. Methods of soil analysis, Chapter 16, *Agronomy, No. 9, Part 1,* 2nd Ed., American Society of Agronomy, 1964, 456 – 478.

[18] Chiou C. T., Rutherford D. W., Manes M., Sorption of N_2 and EGME vapours on some soils, clays, and mineral oxides and determination of sample surface areas by use of sorption data, *Environmental Science Technology, 27,* 1993, 1587 – 1594.

[19] Dias M. I., Suarez M. B., Prates S., MartinPozas J. M., Characterization and acid activation of Portuguese special clays, *Clay Minerals, 38,* 2003, 537 – 549.

[20] Pesquera C., Gonzalez F., Benito I., Blanco C., Mendioroz S., Pajares J., Passivation of a montmorillonite by the silica created in acid activation, *Journal of Material Chemistry, 2(9),* 1992, 907 – 911.

[21] Komandel P., Schmidt D., Medejova J., Cicel J., Alteration of smectites by treatment with hydrochloric acid and sodium carbonate solutions. *Applied Clay Science, 5,* 1990, 113 – 122.