ANALYSIS OF NITRIC ACID ACTIVATED UKPOR KAOLIN: STRUCTURAL TRANSFORMATIONS AND ADSORPTIVE PROPERTIES

*RO Ajemba, V I Ugonabo, PK Igbokwe and OD Onukwuli
Department of Chemical Engineering, Nnamdi Azikiwe University, PMB 5025, Awka, Anambra, Nigeria

ABSTRACT

This study analyzed the structural transformations and adsorption properties of Ukpor clay after nitric acid activation. The clay samples were mined, sun-dried, sized, and reacted with different concentrations of nitric acid ranging from 2 to 16mol/L at various times of 0.5 to 3 hours. The untreated and treated samples were characterized using X-ray Fluorescence and Fourier Transform Infrared (FTIR) Spectroscopy. The adsorptive capacities of the treated samples were investigated by using them to adsorb color pigments from palm oil. The analyses showed that nitric acid leaching caused an exchange of the octahedral cations; Al^{3+}, Fe^{3+}, and Mg^{2+} with H^+ ions and this exchange increased with increase in acid concentration and period of activation. The surface area of the activated samples was observed to increase with increase in concentration and time to about four times that of the raw sample. The adsorption results showed that the adsorptive performance of the modified samples was improved from 27.6% to 85.4%. The equilibrium results fitted Freundlich isotherm model. This study has shown that acid activation led to some structural transformations of Ukpor clay which enhanced the adsorption performance of the clay thereby making it an effective adsorbent for palm oil bleaching.

Keywords: Adsorption, bleaching, surface area, color pigment, isotherm, equilibrium

INTRODUCTION

High cost of mostly used adsorbents such as activated carbons, in the purification and refining of edible and non edible oils, has necessitated for a substitute for them by low cost adsorbents such as clay minerals. Clay minerals, enormously abundant in nature, have been considered as a potential source of adsorbent for removing color 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 (Al-Asheh *et al*., 2003; Chaisena and Rangsriwatananon, 2004), acid activation (Zorica *et al*., 2011; Motlagh *et al*., 2008 and 2011; Taha *et al*., 2011; Eze *et al*., 2012; Folatto *et al*., 2011), treating the cationic surfactants (Wang and Wang, 2008), and polymer modification (Chen *et al*., 2008; Liu, 2007).

Acid activation of clay minerals involves treating the clay with inorganic acids such as H_2SO_4, HCl, or HNO_3 (Diaz and de SouzaSantozs, 2001). The acid activation of clays alters the structural properties, such as, surface area and average pore volume (Doulia *et al*., 2009), and also changes some chemical properties such as cation exchange capacity and surface acidity of the clays, thus, generating the desired characteristics required for an effective adsorbent (Lian *et al*., 2009).

Nigeria is endowed with vast deposits of clay minerals that are unharnessed. The deposit located at Ukpor has not been employed industrially, but, it is only used for local pottery work by the rural inhabitants. This clay mineral can be harnessed and modified to increase its usability in the purification and bleaching of palm oil. 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*. (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

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time. The preparation of acid-activated clay materials must be controlled in order to obtain maximum bleaching capacity (Kirali 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 color reduction from 9.1 % to 27.3%, a poor performance as an adsorbent.

MATERIALS AND METHODS

Materials
Ash-colored clay material from Ukpor (N: 5° 54' 27.5"; E: 6° 56' 3.7"; A: 137m) in Nnewi South, 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 sulphuric 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 2 – 16 mol/L of HNO_3, varying time of 0.5 – 3 hours, and varying temperatures of 70 – 120°C. The clay samples thus prepared were labeled UK0, UK2, UK4, UK8, UK12, UK14, and UK16, 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.

Specific surface area
The surface area was determined using ethylene glycol mono-ethyl-ether (EGME) described by Carter *et al*., (1964 and 1965). 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 (Chiou *et al*., 1993).

Cation Exchange Capacity (CEC) (Ingelthorpe *et al*., 1993)
5 g of the clay sample was weighed into the 250 ml polythene bottle with a magnetic stirrer. The bottle and its contents were weighed (M_1). 100 ml of buffered barium chloride solution was added to the bottle and was placed on a magnetic stirring plate and agitated for 1 hour. At the end of the period, the bottle was centrifuged at 1500 rpm for 15 minutes and the supernatant was discarded. Further 200 ml of the buffered barium chloride solution was added and the mixture was agitated on a magnetic stirring plate for another 1 hour. The bottle and its contents were left overnight. The following day, the bottle and its contents were centrifuged at 1500 rpm for 15 minutes and the supernatant discarded. 200 ml of distilled water was added and agitated for a few minutes on the magnetic stirring plate. It was centrifuged for further 15 minutes and the supernatant discarded. The bottle and its contents were weighed *(M_2)*. 100 ml of $MgSO_4$ solution was pipette into the bottle and stirred well and was left to stand for 2 hours with occasional agitation on the magnetic stirring plate. After 2 hours the contents were centrifuged at 1500 rpm for 15 minutes and the supernatant decanted into the stopper bottle. 5 ml aliquot of this solution was pipette into a 100 ml conical beaker and 5 ml of ammonia buffer and 6 drops of indicator were added to it. This mixture was titrated with standard EDTA (titer A_1 ml). Another titration was done with a 5 ml of

aliquot of 0.05 M $MgSO_4$ solution (titer B ml). The end point was indicated by a blue to pink color change. The Cation Exchange Capacity was calculated as follows:

$$CEC = 8 \left\{ B - \frac{(A_1 \times (100 + M_2 - M_1))}{100} \right\} meq/100g \quad (2)$$

Where M_1 = weight of bottle plus dry content (g), M_2 = weight of bottle plus wet content (g), A_1 = titration end-point of sample (ml), and B = titration end-point of $MgSO_4$ solution (ml)

Bleaching experiment
The bleaching experiments were carried out in a batch process. 50 g of the refined palm oil was 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 color of the bleached oils using a UV-Vis spectrophotometer (Shimadzu UV mini 1240) at a wavelength of 450 nm. The bleaching efficiency of the acid activated clay was calculated in this study using the following equation:

$$\% \, Bleaching \, Efficiency = \frac{(A_{unbleached} - A_{bleached})}{A_{unbleached}} \times 100$$

(3)

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

RESULTS AND DISCUSSION

Characterization
The changes in the chemical composition of the natural and acid activated Ukpor 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 14mol/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 14 mol/L concentration (Fig. 2). The behaviour shown 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 (Dias *et al*., 2003). Pesquera *et al*. (1992) suggest that this free silica generated by the initial destruction of the tetrahedral sheet, is polymerized by the effect of such high acid concentration and is deposited on the undestroyed silicate fractions, thereby protecting it from further acid attack.

Surface area analysis
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 relates to the elimination of the exchangeable cations, de-lamination, and the generation of micro-porosity during the processes (Dias *et al*., 2003). This increase continued up to the sample activated with 14 mol/L of HNO_3 and dropped when the concentration was increased to 16mol/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
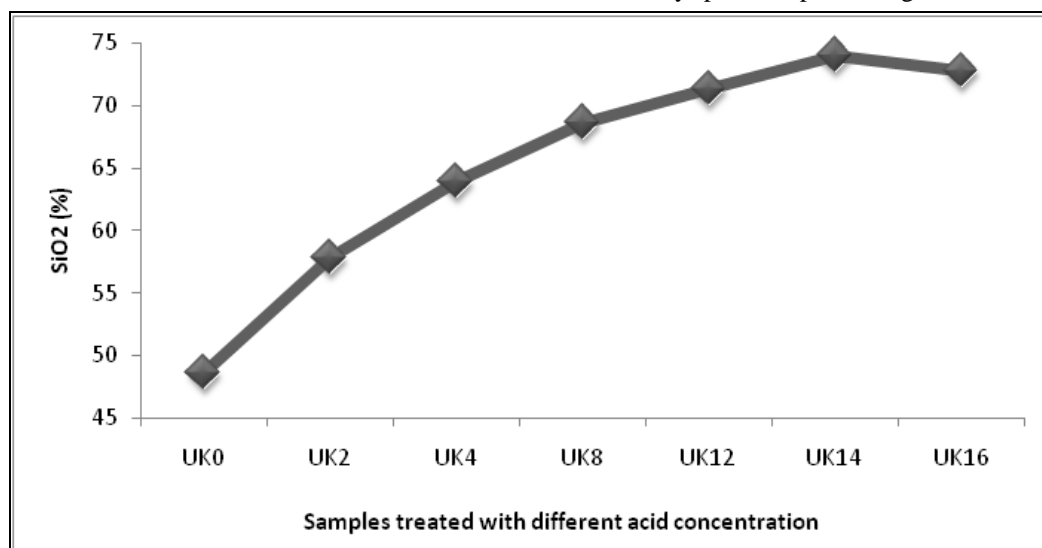

Fig. 1. SiO_2 content of the clay sample after activation with HNO_3 (time = 3 hours, temperature = 120°C).
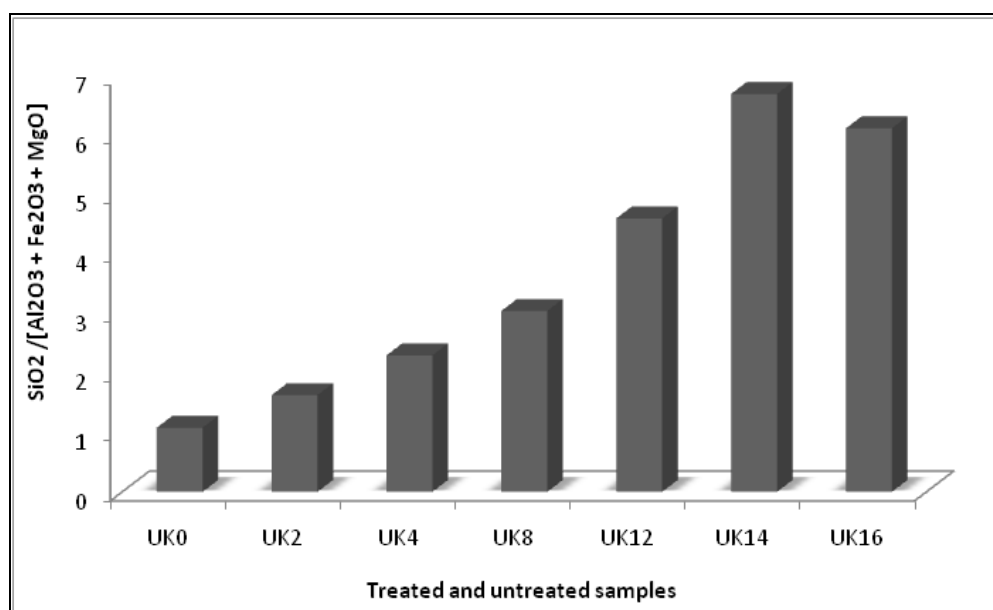
Fig. 2. Variation of SiO_2 / $[Al_2O_3 + Fe_2O_3 + MgO]$ ratios for samples treated with different acid concentrations (time = 3 hours, temperature = 120^oC).

Table 1. Chemical analysis and cation exchange capacity (CEC) of the natural and acid activated Ukpor clay samples determined by XRF.

Chemical composition (%)	Clay samples						
	NT0	UK2	UK4	UK8	UK12	UK14	UK16
Al_2O_3	26.9	21.45	17.04	13.97	9.88	7.16	7.52
SiO_2	48.6	57.8	63.93	68.64	71.36	74.04	72.73
Fe_2O_3	16.13	12.51	9.65	7.83	4.99	3.35	3.85
CaO	0.08	0.05	0.03	0.02	0.02	0.02	0.02
MgO	1.78	1.46	1.08	0.74	0.61	0.52	0.50
K_2O	0.11	0.07	0.05	0.03	0.03	0.03	0.03
TiO_2	2.06	1.74	1.36	1.01	0.84	0.65	0.73
LOI	3.67	2.73	2.25	1.92	1.56	1.21	0.87
Total	99.33	97.81	95.39	94.16	89.29	86.98	86.25
Cation exchange capacity (CEC) (meg/100g)	97	78	63	57	50	46	48

(Pesquera *et al*., 1992). Also, the surface area increase as the acid concentration increased is attributed to the reduction in the contents of the octahedral cations of Al^{3+}, Fe^{3+}, and Mg^{2+}, and the increase in the ratio of SiO_2 / $(Al_2O_3 + Fe_2O_3 + MgO)$ as in figure 4.

Fourier Transform Infrared (FTIR) spectroscopy analysis
The spectra of the untreated and the sample treated with 14 mol/L HNO_3 are shown in figures 5 and 6, respectively. 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 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 adsorptive bands attributed to the OH vibrations and octahedral cations. The intensities of the stretching bands observed at 3449, 1639, and 792 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 3692, 3525, and 1104 cm^{-1} assigned to the H-O-H stretching. The peak assigned to Si-O-Si stretch at 472, 685, 920 and 1037, 1037, 3626 cm^{-1} remained after acid leaching with slight increase in the intensities, similar result was reported by others (Christidis *et al*., 1997;
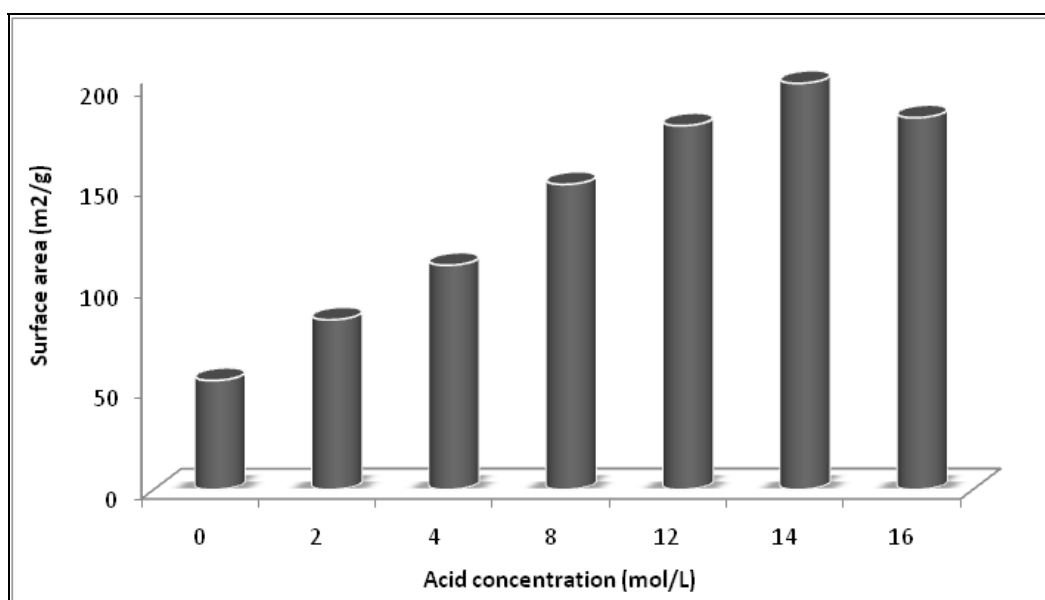
Fig. 3. Variation of the surface area with acid concentration used in activation of the samples (time = 3 hours, temperature = 120°C).
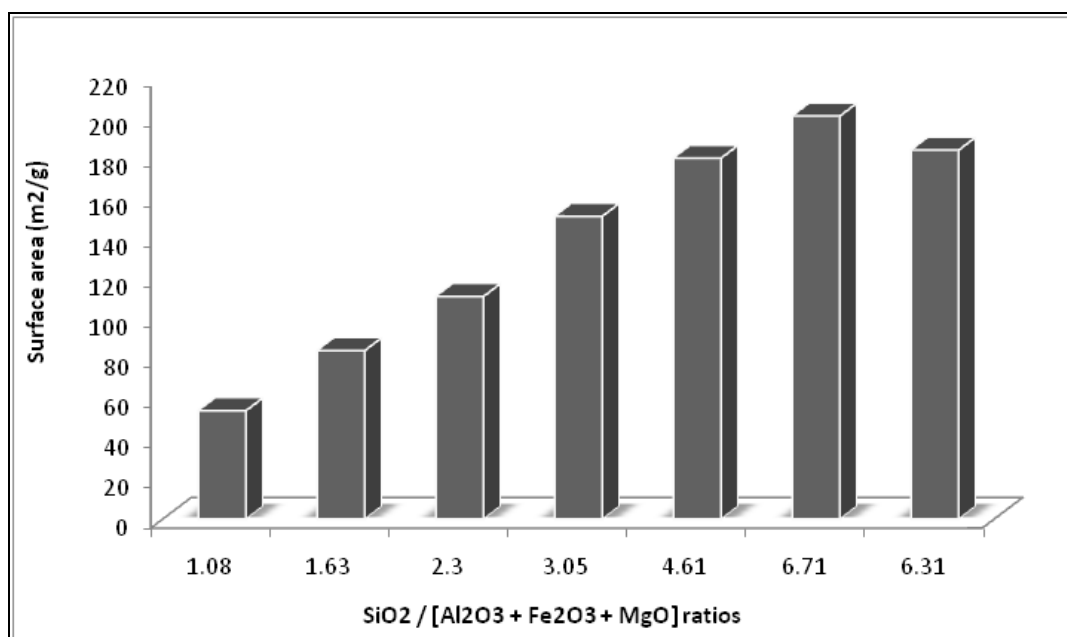

Fig. 4. Variation of surface area with change in SiO$_2$ / [Al$_2$O$_3$ + Fe$_2$O$_3$ + MgO] ratios.

Komadel *et al*., 1990). The transformation of the tetrahedral occurred at 720 cm^{-1} which was increased after the acid treatment.

Effect of activation time on the clay samples
The activation experiment was performed at various times ranging from 0.5 to 3 hours. The results of the studies are depicted in figure 7. The figure shows that the surface area increased as the time of activation increased alongside the acid concentration. The prolonged period of

activation allowed for maximum contact between the clay mineral and the acid molecules which aided the dissolution of the cations from the octahedral layer (aluminium, ferric, and magnesium ions). These ions then replaces the alkaline earth cations (Ca^{2+}, Na$^+$, and K$^+$) in the interlayer region, and this led to increase in surface area and porosity as a result of the inaccessible sites within the clay structure that were opened up (Taylor, 2005).
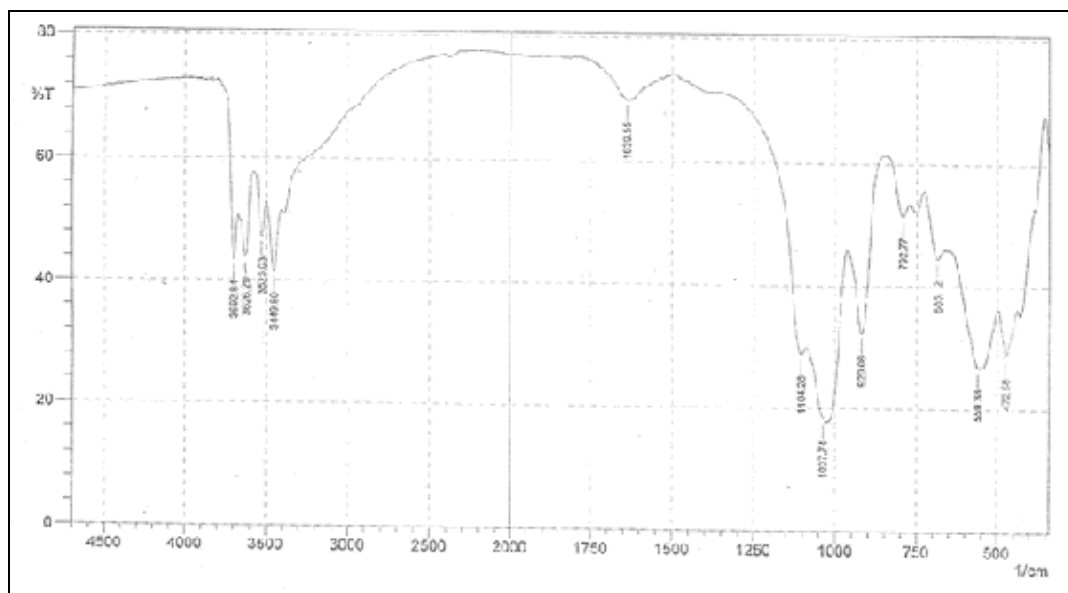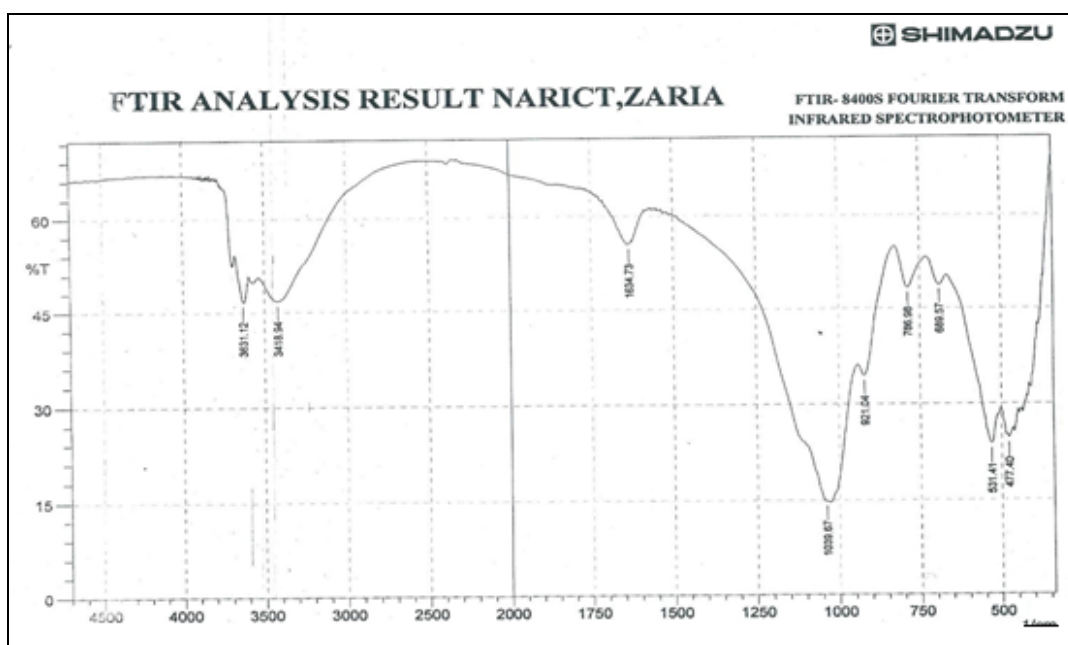
Fig. 5. FTIR spectrum of untreated Ukpor clay sample.

Fig. 6. FTIR spectrum of Ukpor clay sample treated with 14 mol/L of HNO_3.

Bleaching Studies

The results of the bleaching studies performed using the natural and acid activated samples are shown in figure 8. The figure shows that the bleaching efficiency increases with an increase in the acid concentration used in the activation step. The increase reached a maximum with the sample activated with 14mol/L HNO_3 and decreased thereafter with further increase in the acid concentration. This decrease in bleaching efficiency is attributed to the

small surface area and high $Al_2O_3 + Fe_2O_3 + MgO$ content exhibited by the sample activated with 16mol/L of HNO_3 that led to the destruction of the clay crystalline structure as shown in figure 9.

Adsorption Isotherms

The mechanism of adsorption of the color pigments onto the acid modified Ukpor clay was determined by evaluating the equilibrium data obtained from the
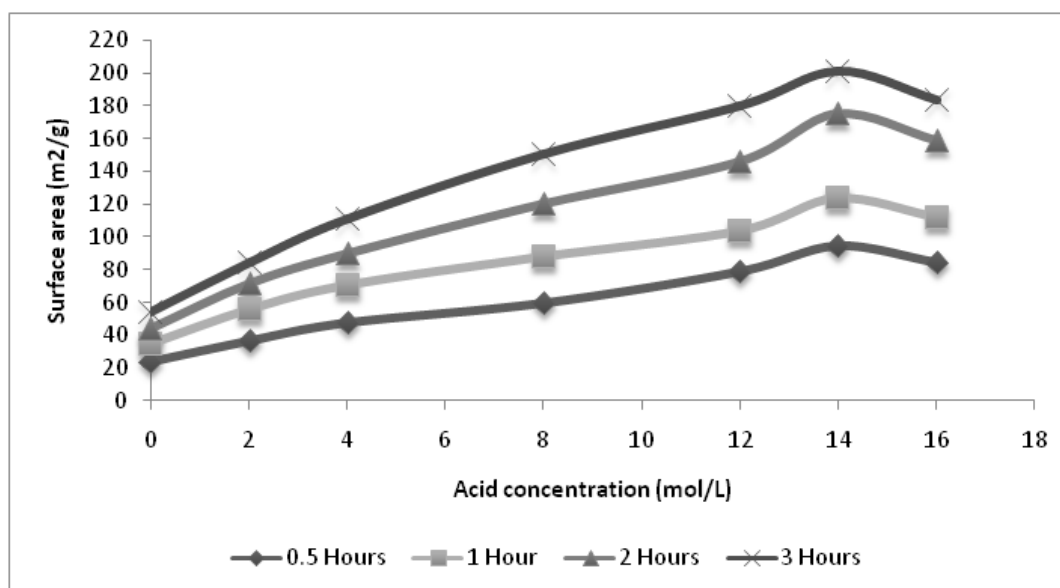
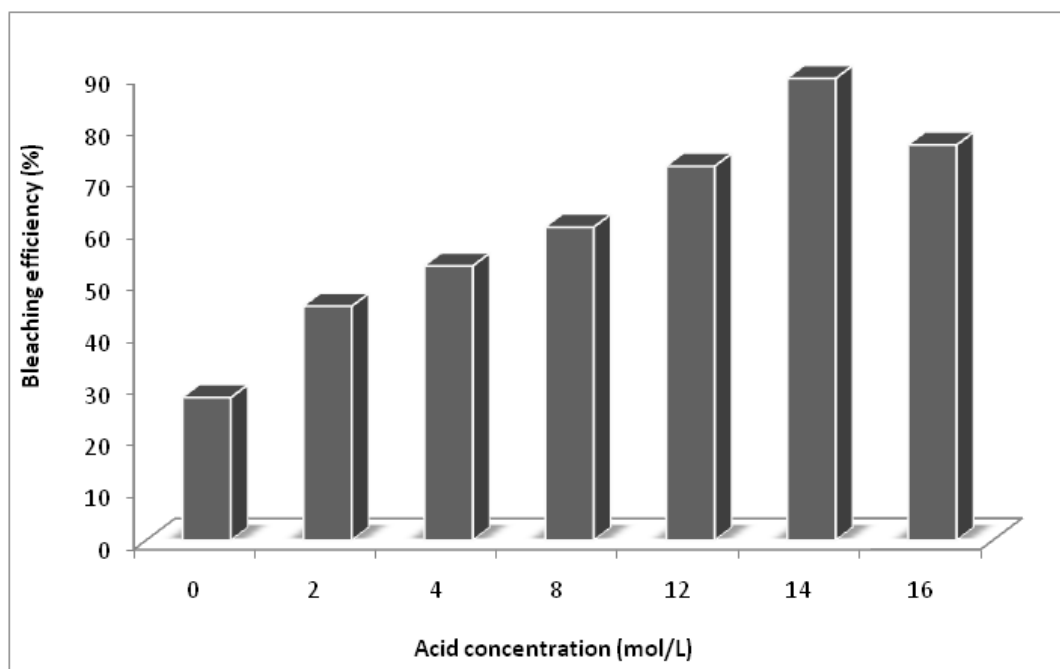Fig. 7. Variation of surface area with time at different acid concentrations.

Fig. 8. Variation of the bleaching efficiency with acid concentrations used in the activation (time 3 hours, temperature 120°C).

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 color 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:

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

Where C_e is the equilibrium concentration of the pigments (mg/l), q_e is the amount of color 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 the intercept of
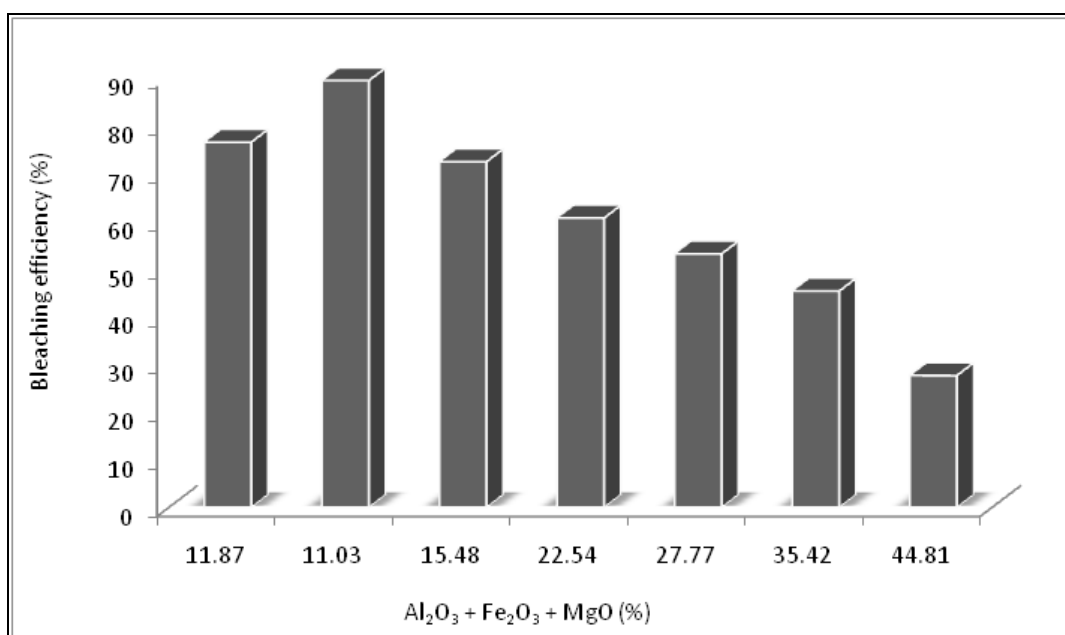
Fig. 9. Variation of the bleaching efficiency with $Al_2O_3 + Fe_2O_3 + MgO$ content.
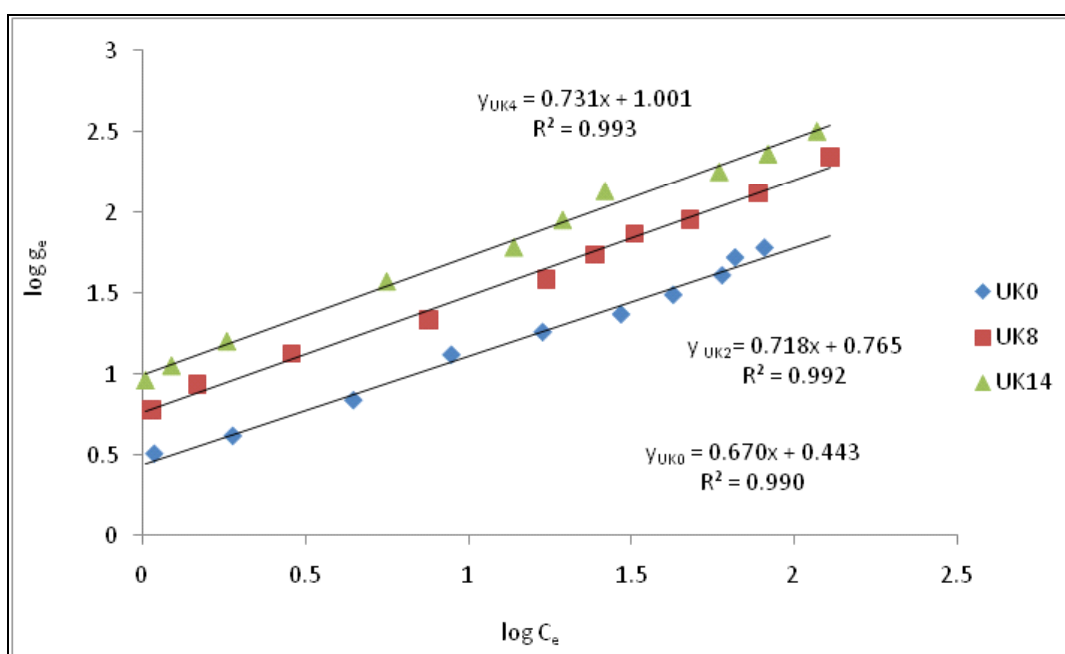

Fig. 10. Freundlich adsorption isotherm for colour pigment adsorption onto acid modified Ukpor clay.

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:

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

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 figure 10 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 color pigments onto acid modified Ukpor clay occurred in multi-layer.

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

Isotherm Model	Model Parameters	Clay Type		
		UK0	UK8	UK14
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

CONCLUSION

The analysis of the structural and adsorptive effects of nitric acid activation of Ukpor clay has been successfully investigated. The results showed that the acid activation caused physical and chemical modifications on the treated clay samples. The structural properties affected are surface area, adsorption capacity, and cation exchange capacity. The activated samples exhibited a high adsorptive capacity thereby affirming the effectiveness of the acid treatment. The surface area was observed to increase with an increase in the acid concentration and reaction time. The equilibrium study showed that the prepared adsorbent adsorbed in multi-layers in accordance with Freundlich isotherm model. It can then be concluded that acid activation of Ukpor kaolin enhances its adsorptive capacity and makes it an effective adsorbent for palm oil bleaching.

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