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# Investigation of the Effects of Sulphuric Acid Modification on the Structural and Bleaching Performance of Ukpor Clay

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## ABSTRACT

The effects of sulphuric acid modification on the structural and bleaching performance of Ukpor clay were investigated. The clay samples from Ukpor were mined; washed; sun-dried; sized to 0.075mm particle size and reacted with different concentrations of sulphuric acid ranging from 1M to 6M. The raw and acid modified samples were characterized using X-ray Fluorescence and Fourier Transform Infrared Spectroscopy (FTIR) to investigate the effects of acid leaching. The adsorptive performance of the modified samples was investigated by using the samples to remove colour pigments from palm oil. The analyses showed that sulphuric 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 modified samples was 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 with the sample modified with 4M $H_2SO_4$ given the best result. The adsorptive capacity increased from 28.4% (using the raw clay sample) to 79.5% (using the 4M $H_2SO_4$ modified sample). The equilibrium result showed that the colour pigment adsorption onto acid modified Ukpor clay occurred in multi-layer in agreement with Freundlich adsorption isotherm model. Conclusively, this study has shown that sulphuric acid modified Ukpor clay is a good adsorbent for palm oil bleaching and that acid concentration is an important factor in the modification step.
**KEYWORDS:** modification; adsorption; sulphuric acid; palm oil; Ukpor clay; bleaching.

## INTRODUCTION

Alumino-silicate materials, 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 Ukpor 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 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.

The main focus of this study is to investigate the structural effects of sulphuric acid modified Ukpor clay by exploring surface area and structural changes via a series of tests like X-ray fluorescence and Fourier transform

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infrared spectroscopy. The acid modified clay samples are to be used for the adsorption of colour pigments from palm oil.

## MATERIALS AND METHODS

### Materials

Ash-coloured clay material from Ukpor (N: 5° 54’ 27.5”; E: 6° 56’ 3.7”; A: 137m) in Nnewi 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 0.075 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 $^0$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 1 – 6M 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 UK0, UK1, UK2, UK3, UK4, UK5, and UK6, 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 also measured.

### 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 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:

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

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

## RESULTS AND DISCUSSIONS

### Characterization

The changes in the chemical composition, specific surface area and maximum bleaching efficiency of the natural and acid activated Ukpor clay as a function of acid concentration are shown in Table 1.

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

| Chemical composition (%) | Clay samples | | | | | | |
|---|---|---|---|---|---|---|---|
| | UK0 | UK1 | UK2 | UK3 | UK4 | UK5 | UK6 |
| $Al_2O_3$ | 23.9 | 21.64 | 20.93 | 19.56 | 17.04 | 16.76 | 16.13 |
| $SiO_2$ | 58.60 | 63.86 | 65.83 | 66.37 | 67.23 | 68.53 | 69.20 |
| $Fe_2O_3$ | 10.13 | 8.23 | 7.45 | 6.63 | 5.91 | 5.09 | 4.65 |
| CaO | 2.08 | 1.08 | 0.96 | 0.85 | 0.80 | 0.78 | 0.76 |
| MgO | 1.03 | 0.58 | 0.50 | 0.47 | 0.43 | 0.40 | 0.37 |
| $K_2O$ | 0.12 | 0.05 | 0.04 | 0.03 | 0.03 | 0.02 | 0.02 |
| LOI | 4.14 | 3.76 | 3.01 | 2.87 | 2.31 | 2.03 | 1.87 |
| Surface area ($m^2/g$) | 58 | 148 | 162 | 185 | 226 | 239 | 233 |
| Max. Bleaching efficiency (%) | 28.4 | 65.7 | 69.5 | 72.8 | 79.5 | 74.6 | 70.7 |
| Si/(Al + Fe + Mg) | 1.67 | 2.09 | 2.28 | 2.49 | 2.88 | 3.08 | 3.27 |

Variations in the chemical composition of the samples are indications that acid activation modifies the structure of the clay minerals. From the table, the following conclusions can be drawn:

- As the concentration of the acid treatment increases, the decolourizing ability for the refined oil increases up to an optimum value, but with further treatment there is a decline in that ability.
- As the concentration of the acid treatment is increased, the specific surface area increased up to a maximum value, which decreases with further increase in the intensity of the acid treatment.
- As the concentration of the acid activation increases, the rate of dissolution of $Ca^{2+}$, $Na^{+}$, and $K^{+}$ were high after leaching with 1M $H_2SO_4$ and the rate decreased as the treatment concentration increased, while the dissolution rate of $Fe^{2+}$, $Mg^{2+}$, and $Al^{3+}$ were slow even at higher acid activation intensity.
- The maximum bleaching efficiency does not correspond to the maximum surface area value. As can be observed from Table 1, UK5 has a surface area of $239 m^2/g$ and a maximum bleaching efficiency of 74.6%, while UK4 has a surface area of $226 m^2/g$ with a maximum bleaching efficiency of 79.5%. Naturally, UK5 should be expected to have higher bleaching efficiency as a result of higher surface area value. It has been reported by researchers [16, 17, 18] 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.
- The acid activation of the clay samples increased the amount of silica ($SiO_2$) content, but the increase was more at lower acid concentration. The analyses of the results in the table show decrease in the relative amount of cations belonging to the octahedral sheet and increase in the Si/Al + Fe + Mg ratio.

The chemical changes that took place in the clay structure as a result of acid modification lead to existence of vacancies in the lattice. This led to the increase in the adsorptive ability of the acid modified clay samples. In order to provide charge equilibrium, as a result of acid modification, the hydrogen ion from the acid replaces the exchangeable cations like $Na^{+}$ and $Ca^{2+}$ that are present in the clay layer.

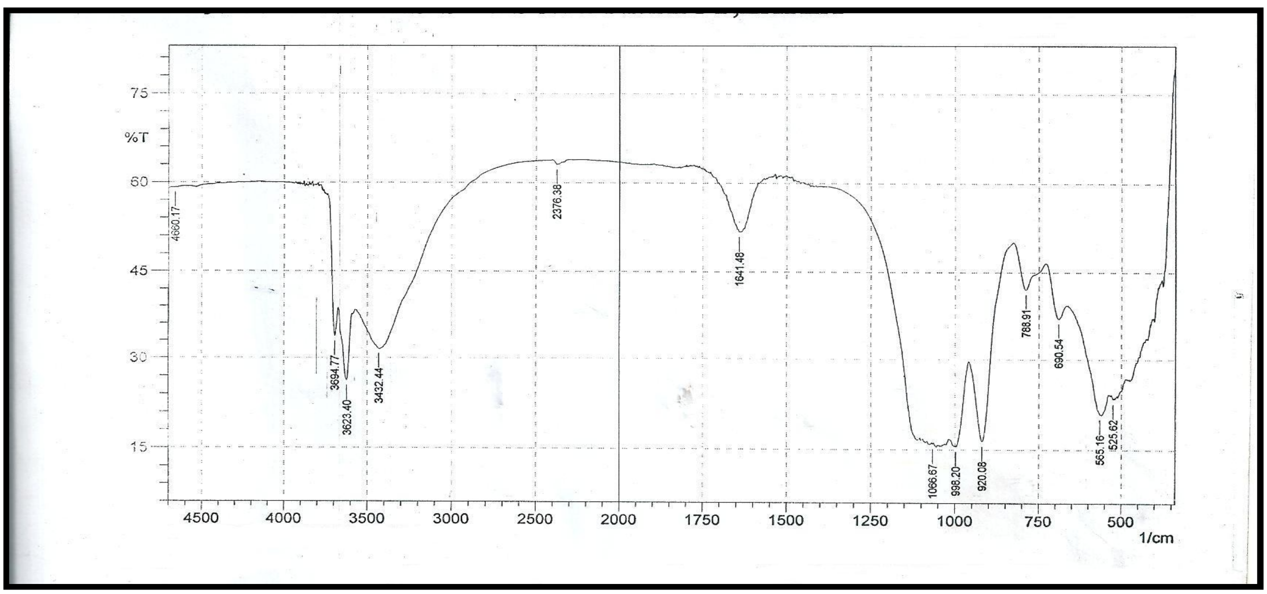


Figure 1: FTIR spectrum of natural Ukpor clay

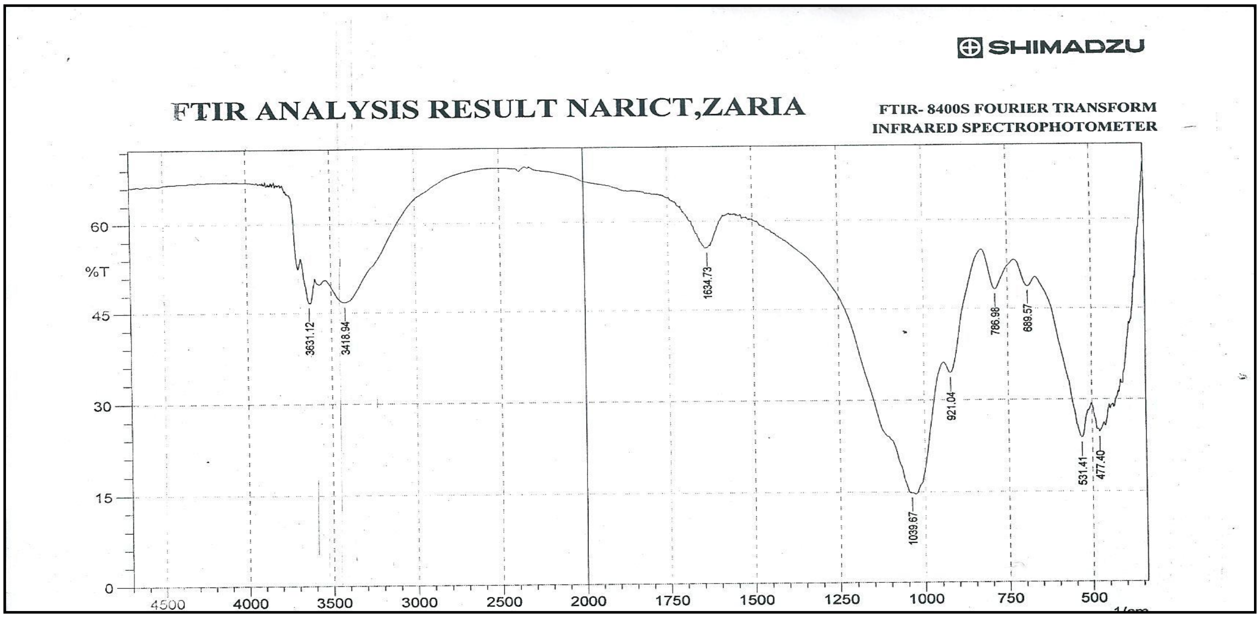


Figure 2: FTIR spectrum of 4M $H_2SO_4$ acid modified Ukpor clay

The FTIR spectra of the untreated and treated clay samples are shown in Figures 1 and 2, respectively. Comparing Figures 1 and 2, it is clear that there were some structural modifications on the clay sample as a result of acid activation. The untreated clay sample shows absorption bands at 525, 565, 690, 788, 920, 998, 1066, 1641, 2376, 3432, 3623, 3894, and 4660 $cm^{-1}$. The positions and assignments of these vibrational bands of the dioctahedral clay are shown in Table 2, both for the untreated and treated clay samples. Some of the bands were removed or shifted after the acid activation (Figure 2) and their intensities also changed. This indicates that there is a minimal damage to the crystal structure of the clay material. This result is in agreement with the findings of other researchers [6, 19-21].

Table 2: FTIR spectra band for natural and activated clay samples and their possible assignments

| **Spectra band ($cm^{-1}$)** | | **Assignment** |
|---|---|---|
| **Natural sample** | **Activated sample** | |
| **525** | 477 | O-Si-O bend |
| **565** | 531 | Si-O-Al/Fe-O stretch |
| **690** | 689 | Al-O-Si/Fe-O bond |
| **788** | 786 | Si-O bend/ C-O bond |
| **920** | 921 | Al-O-Si stretch |
| **998** | - | Si-O-Si stretch |
| **1066** | 1039 | Si-O/Si-O-Si |
| **1641** | 1634 | Al-O-H stretch |
| **2376** | - | Al-O-Si stretch |
| **3432** | 3418 | H-O-H stretch |
| **3623** | 3631 | O-H stretch |
| **3894** | - | H-O-H bend |
| **4660** | - | O-H stretch |

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 $Al_2O_3$ + $Fe_2O_3$ + MgO in the samples. Figure 3 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 ($Al_2O_3$ + $Fe_2O_3$ + MgO) content decreases and this reached a maximum at which the surface area decreased with decrease in the octahedral oxides.

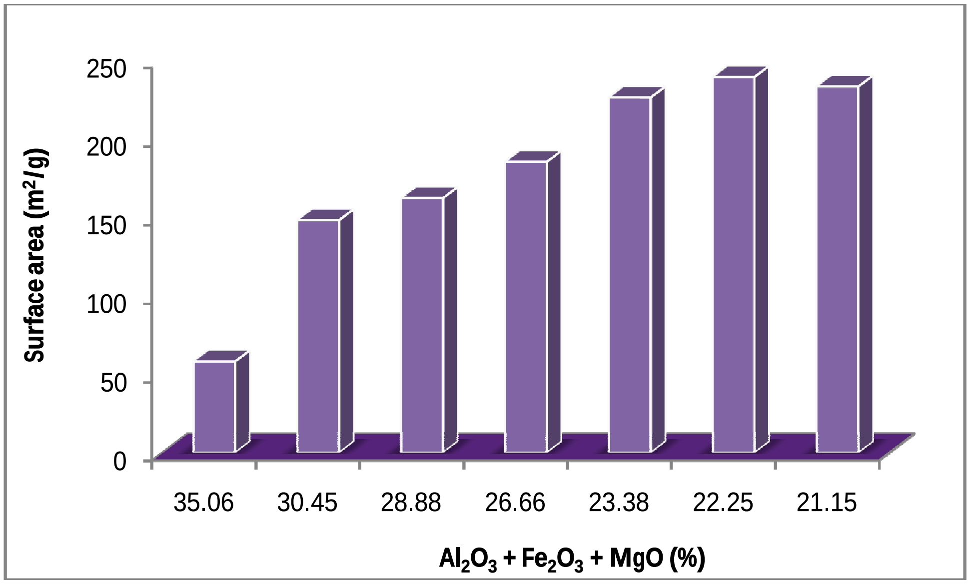


Figure 3: Variation of the surface area with the amount of $Al_2O_3 + Fe_2O_3 + MgO$.

Figure 4 shows the dissolution of the cations from the clay layer as the acid concentration increased. From the figure it is clear that the cations $Ca^{2+}$ and $K^+$ are easily removed at lower acid concentration, while the cations $Al^{3+}$, $Fe^{3+}$, and $Mg^{2+}$ are removed appreciably at higher acid concentration.

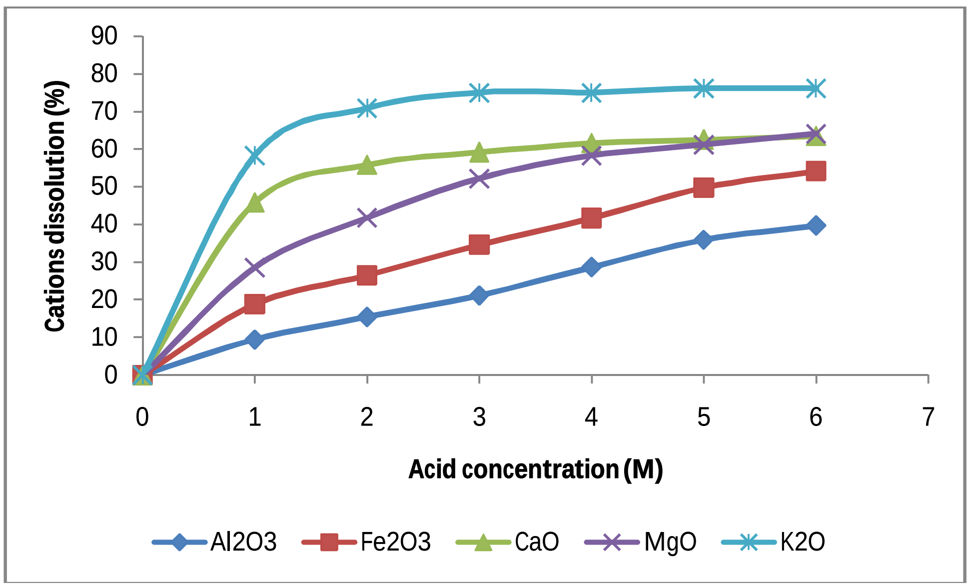


Figure 4: Cation dissolution at different acid concentrations.

**Bleaching efficiency**

The results of the bleaching studies performed using the natural and acid-modified 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 modified with 5M 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, UK4 has a surface area of $226m^2/g$ and a maximum bleaching efficiency of 79.5%, while UK5 has a surface area of $239m^2/g$ with a maximum bleaching efficiency of 74.6%. Naturally, UK5 should be expected to have higher bleaching efficiency as a result of higher surface area value. It has been reported by researchers [16-18] that the optimum decolourizing ability of modified 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.

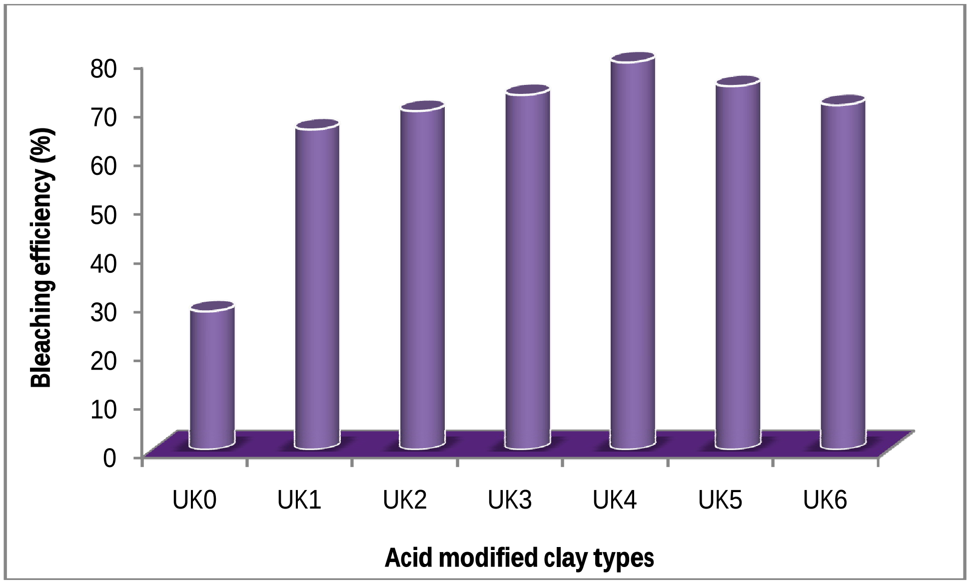


Figure 5: Plot of bleaching efficiency versus the modified clay type.

**Adsorption Isotherms**

The mechanism of adsorption of the colour pigments onto the acid modified Ukpor 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;

$$C_e/q_e = C_e/q_m + 1/\,(K_L q_m) \qquad (2)$$

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 3.

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;

$$\log q_e = \log k_f + 1/n\,(\log C_e) \qquad (3)$$

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 6 and the values are presented also in Table 3. A comparison of the values of the coefficient of determination ($R^2$) shown in Table 3, 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 Ukpor clay occurred in multi-layer.

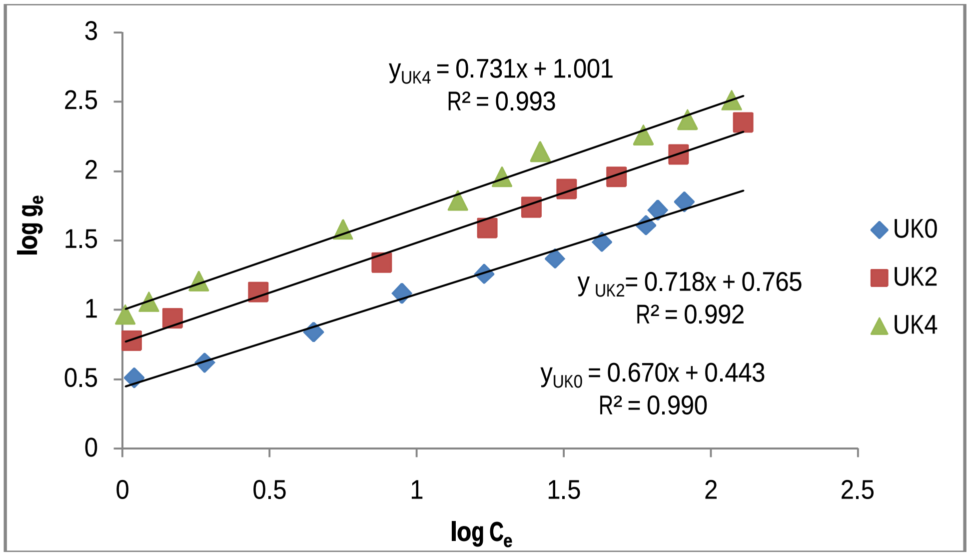


Figure 6: Freundlich adsorption isotherm for colour pigment adsorption onto acid modified Ukpor clay.

Table 3: Freundlich and Langmuir isotherm constants and the respective correlation coefficients

| **Isotherm Model** | **Model Parameters** | **Clay Type** | | |
|---|---|---|---|---|
| | | UK0 | UK2 | UK4 |
| **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 effect of sulphuric acid modification on the structural properties and bleaching performance of Ukpor clay has been successfully investigated. The structure of the clay was modified by the acid-leaching process and the bleaching efficiency was increased from 28.4 to 79.5%. Based on the results activated clay from Ukpor performs better than the un-activated one and the acid concentration plays an important role in the activation step. The equilibrium studies showed that the adsorption of colour pigment from palm oil onto acid modified Ukpor clay occurs in multi-layer in agreement with the Freundlich adsorption isotherm model. It can be deduced from this study that high performance adsorbent for palm oil bleaching can be produced from Ukpor clay via acid modification.

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