Modification of the physico-chemical properties of udi clay mineral to enhance its adsorptive capacity

Regina O. Ajemba

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

ABSTRACT

The Physico-chemical properties of Udi clay mineral were modified in this work to increase its adsorptive performance. The Udi clay was mined from Eke town, separated from dirt, washed, sun-dried, and grinded to a particle size of 0.045mm. The modification of the sized samples were done by two physico-chemical methods; thermal activation at different temperature range of 100 to 500 ^0C and acid activation at different concentrations of sulphuric acid ranging from 2 to 10M. The physicochemically modified samples were characterized using X-ray fluorescence, Fourier transform infrared (FTIR) spectroscopy, and Brunner-Emmet-Teller (BET) method for surface area. The modified samples were used to bleach palm oil to investigate their adsorptive performance. The equilibrium data were analyzed using Langmuir and Freundlich adsorption isotherms. Results of the characterization showed that the modified samples had more surface area and adsorptive capacity than the raw samples. The surface area was increased to more than three times and four times that of the raw sample for the thermal and acid activated samples, respectively. The bleaching efficiency increased from 29.67% to 75.3% and 92.74%, for thermally and acid activated samples, respectively. Results of the equilibrium analysis showed that the adsorption of colour pigment onto the thermally and acid modified samples occurred in multi-layer in agreement with Freundlich isotherm model. This study has shown that local clay from Udi can be thermally and chemically activated to modify the physico-chemical properties which increase its adsorptive capacity.

Keywords: Activation, adsorbent, bleaching, palm oil, Udi clay, sulphuric acid
_____

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 [1]. 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 [2], [3], acid activation [4], [5], [6], [7], [8], [9], treating the cationic surfactants [10], and polymer modification [11], [12]. Thermal activation of clay mineral is a physical treatment which involves calcination of clays at high temperatures [3] and it is done in order to remove any impurities or moisture attached to

2042

_____

the clay particles [13]. The acid activation of clay minerals is normally done by treating them with HCl, H_2SO_4, or HNO_3 [14]. Acid activation alters the physical properties, such as, enhancing the surface area and average pore volume [15]. It also changes the chemical properties such as cation exchange capacity and the surface acidity of the clays, thus, generating the desired characteristics required for an effective adsorbent [16]. Adsorption is a well known process which many authors have investigated using high-cost adsorbents such as activated carbon [17], [18], [19], [20]. Nigeria is endowed with vast deposits of clay minerals that are unharnessed. The deposit located at Udi 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 [21].

In this work, the aim is to modify the physicochemical properties of local clay from Udi (Nigeria) to enhance its adsorptive capacity. This was achieved by calcination and acid activation of the clay mineral. The characteristics of the modified clay samples were analyzed and also, the adsorptive performance of the modified samples was investigated by bleaching palm oil.

MATERIALS AND METHODS

Materials
Ash-coloured clay material from Udi (N: 6° 31' 00"; E: 7° 43' 00"; A: 327m) in Udi local government area of Enugu 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.

Thermal activation of the clay sample
The physical modification of the clay material was done by thermal activation. The mined clay was washed, sun-dried for 24 hours and grinded to 0.212mm particle size. 20 g of the sized sample was measured into a crucible and placed in a murfle furnace. The thermal activation was performed over a temperature range of 100 to 500 ^{0}C (100, 200, 300, 400, and 500 ^{0}C) for a fixed period of 90 minutes. At the completion of the activation duration, the samples were taken out and cooled in a desiccator for 4 hours. The samples were labeled UD0, UD100, UD200, UD300, UD400, and UD500 where the numbers indicate the calcination temperatures used in the study.

Acid activation of the clay sample
The clay material was prepared for activation by sun-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 ^{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 0.212 mm particle size. The activation process was repeated with varying acid concentrations of 2 – 10M 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 UD0, UD2, UD4, UD6, UD8, and UD10, 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_2 gas.

Adsorption experiment
The adsorption 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 modified (thermal and acid activated) clay samples were also added in turn. 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 and thermally 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 and thermally modified clay samples were calculated in this study using the following equation:

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

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

RESULTS AND DISCUSSION

Characterization
Thermal activation
The results of the chemical analyses of the thermally activated Udi clay samples are given in Table 1. The results indicated that the main chemical compositions are oxides of Al, Si, and Fe, together with other mineral oxides of K, Na, Mg, Ca, and others. Comparison of the calcined samples with the raw sample showed an increase in these oxides as the temperature of calcination increases up to 300 ^{0}C and thereafter remained constant with further increase in temperature. This could be attributed to complete removal of water and organic substances from the clay structure.

Table 1: The chemical composition, bleaching efficiency, surface area, and Si/Al + Fe + Mg ratios of thermally activated and raw Udi clay determined by XRF

Chemical composition	Clay samples					
	UD0	UD100	UD200	UD300	UD400	UD500
Al_2O_3	24.10	25.34	26.11	26.20	26.23	26.19
SiO_2	48.70	53.65	55.74	56.84	56.92	56.87
Fe_2O_3	11.38	12.21	12.56	12.61	12.62	12.61
CaO	0.51	0.51	0.51	0.51	0.51	0.51
MgO	5.20	6.35	6.58	6.63	6.62	6.62
K_2O	1.35	1.45	1.49	1.51	1.50	1.49
TiO_2	2.35	2.57	2.59	2.63	2.62	2.62
Na_2O	0.04	0.05	0.05	0.05	0.05	0.05
Surface area (m^2/g)	87.7	98.7	135.5	197.6	175.6	153.2
Max. Bleaching efficiency (%)	29.5	41.6	58.4	75.3	64.4	60.7
Si/(Al + Fe + Mg)	1.20	1.22	1.23	1.25	1.25	1.25

Results of the adsorption studies on the thermally activated samples in bleaching palm oil are shown in Figure 1. The Figure shows that the adsorption efficiency increased with temperature up to 300 ^{0}C and dropped with further increase in calcination temperature. This is in line with the data in Table 1; the thermally activated sample at 300 ^{0}C had the most surface area and therefore adsorbed more pigments than the other samples.

Acid activation analysis
The results of the x-ray fluorescence analysis of the raw and acid activated clay samples are shown in Table 2. 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 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 [6]. More of the exchangeable cations were easily removed under mild treatment with the acid; such cations include Ca^{2+} and K^+. Their dissolution remained almost constant after treating with 4M acid concentration. The dissolution of the octahedral cations (Al^{3+}, Fe^{3+}, and Mg^{2+}) was continuous as the acid concentration increased.
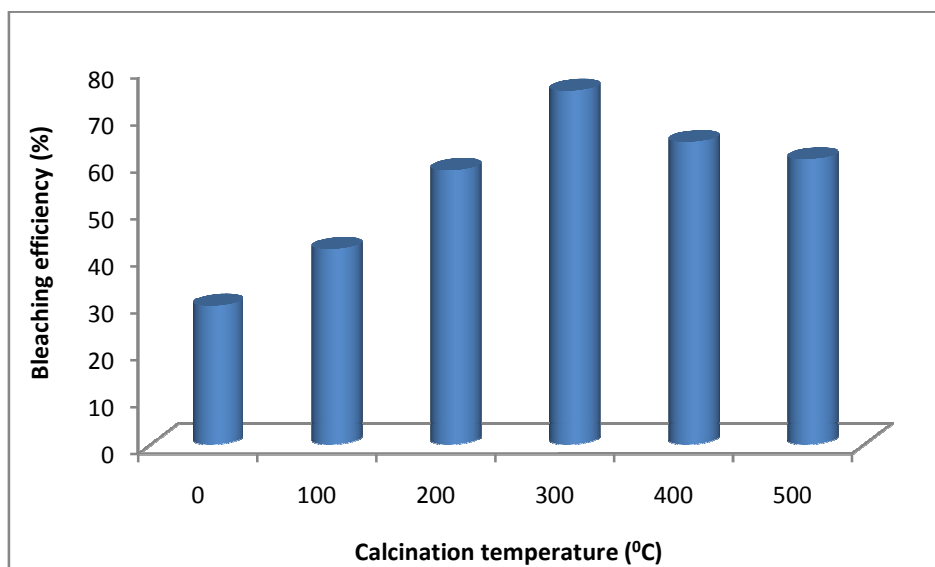
_____

Figure 1: Variation of the bleaching efficiency with calcination temperature.

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 (K^+, Na^+, and Ca^{2+}) with hydrogen ions and leaching of Al^{3+}, Fe^{3+}, and Mg^{2+} from the octahedral and tetrahedral sites which exposes the edges of the cay particles [22]. Further increase in the acid concentration beyond 8M of H_2SO_4 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 Al^{3+}, Fe^{3+}, and Mg^{2+}, resulting in the collapse of the layered crystalline structure of the clay material [23].

Table 2: Chemical analysis, specific surface area, maximum bleaching efficiency and cation exchange capacity (CEC) of the natural and acid activated Udi clay samples determined by XRF

Chemical composition (%)	Clay sample					
	UD0	UD2	UD4	UD6	UD8	UD10
Al_2O_3	24.10	19.22	16.74	13.96	10.97	8.52
SiO_2	48.70	58.94	63.62	68.65	70.32	72.67
Fe_2O_3	11.38	8.23	6.17	4.38	3.09	2.01
CaO	0.51	0.26	0.13	0.09	0.05	0.05
MgO	5.20	3.75	2.17	1.23	0.99	0.68
K_2O	1.35	0.98	0.72	0.65	0.61	0.60
TiO_2	2.35	1.14	1.08	0.84	0.53	0.44
MnO	0.35	0.15	0.09	0.04	0.01	0.01
CuO	0.30	0.16	0.10	0.05	0.05	0.05
Na_2O	0.04	0.02	0.01	0.01	0.01	0.01
LOI	5.34	3.41	2.04	1.87	1.46	1.09
Surface area (m^2/g)	87.7	198.4	256.9	336.7	363.53	359.6
Max. Bleaching efficiency (%)	29.5	52.7	63.8	77.53	92.74	83.9
Si/(Al + Fe + Mg)	1.20	1.89	2.54	3.51	4.67	6.48
Cation exchange capacity (CEC), meg/100g	98	76	63	54	50	49

Fourier Transform Infrared (FTIR) analysis
The FTIR spectra of the untreated and UD8 acid treated clay samples are shown in Figures 2 and 3, respectively. Comparing Figures 2 and 3, 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 472.58, 559.38, 685.20, 792.77, 920.08, 1037.74, 1104.28, 1639.55, 3449.80, 3525.03, 3626.29 and 3692.04 cm^{-1}. After acid treatment, the bands at 3692.04 and 3626.29 cm^{-1} attributed to the O – H stretching of Kaolinite were modified to 3694 and 3623.40 cm^{-1}, respectively. The vibrational bands at 3525 and 1104 cm^{-1} associated with Al – O – Al were completely absent after

2045

_____

acid activation, while bands at 1037, 920, 792, 685, and 559 cm^{-1} related to the Si – O – Si and O – Si – O stretching remained after acid leaching. This verifies the x-ray fluorescence analysis report that the Si^{+4} ion increases with acid treatment while the octahedral cations Al^{3+}, Fe^{3+}, and Mg^{2+} decreases with acid activation. 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 [2], [7], [24], [25], [26], [27].
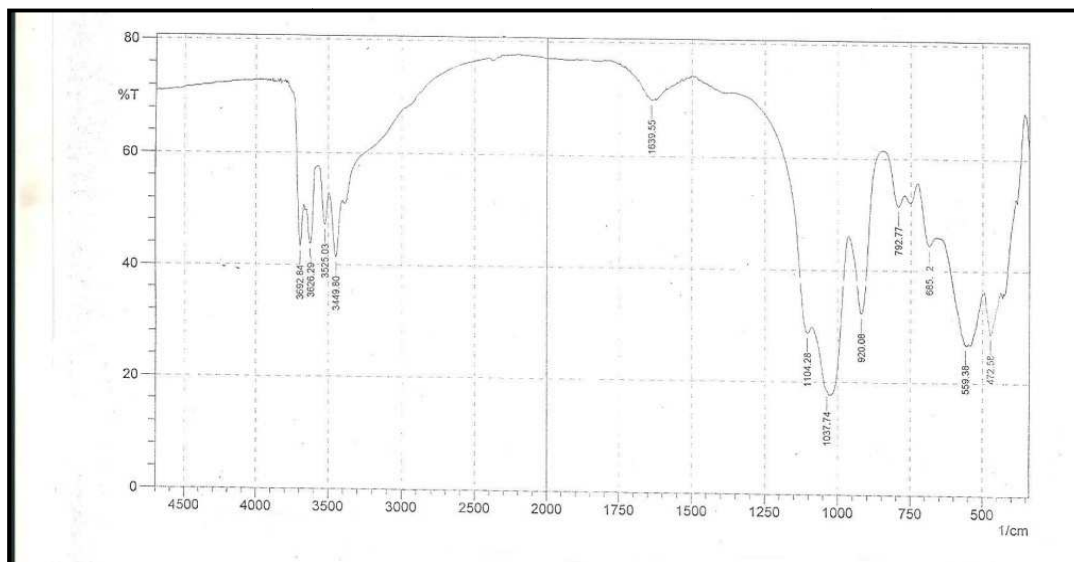
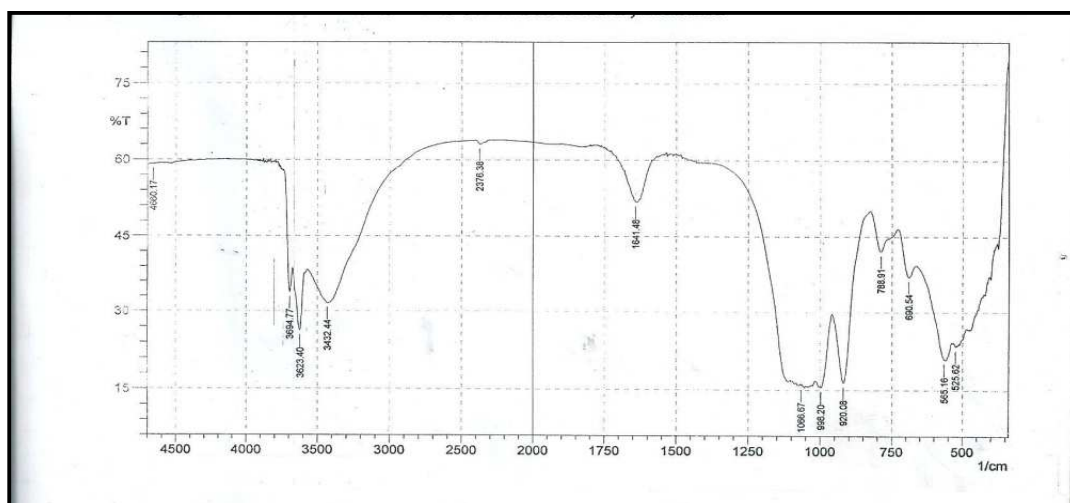**Figure 2: FT-IR spectra of natural Udi clay.**

Figure 3: FT-IR spectra of acid modified Udi clay.

Bleaching efficiency of the acid activated sample
The bleaching results obtained using the acid modified samples in adsorbing colour pigment from palm oil are shown in Figures 4 and 5. Figure 4 shows the variation of the bleaching efficiency as a function of acid concentration while Figure 5 shows its variation with respect to the Si/ [Al + Fe + Mg] ratio. Both figures depict that bleaching efficiency increases as the acid concentration and Si/ [Al + Fe + Mg] ratio increases up to 8M of acid concentration and 4.67 of Si/ [Al + Fe + Mg] ratio, above these values the bleaching efficiency dropped. This is as a result of partial destruction of the clay structure by the excess acid and also explains the conversion of meso-porous to macro-porous [7], [22].
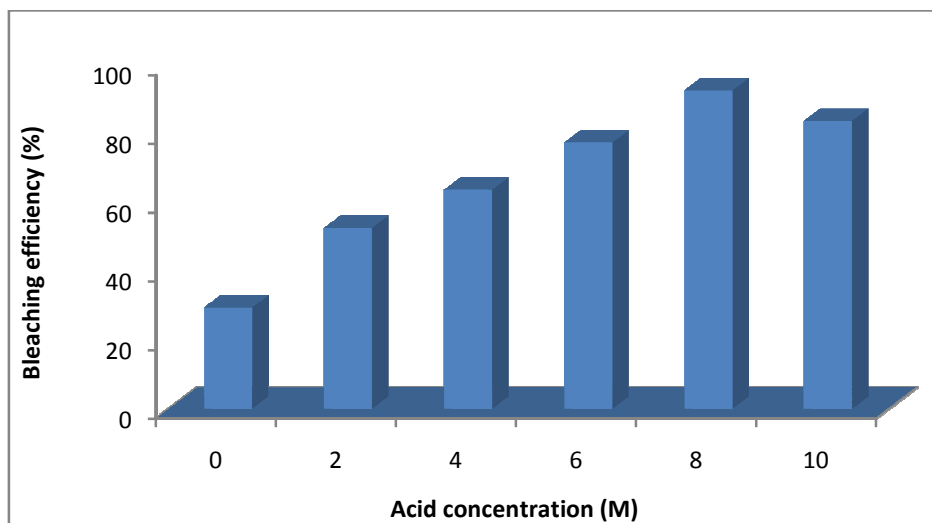
_____

Figure 4: Variation of bleaching efficiency with acid concentration.
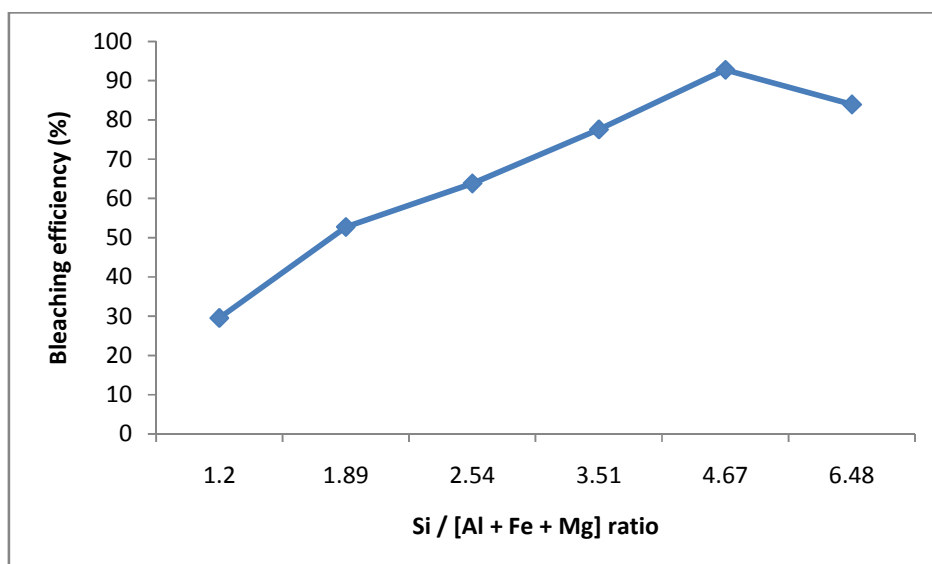

Figure 5: Variation of bleaching efficiency with Si / [Al + Fe + Mg] ratio.

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;

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

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;

$$\log q_e = \log k_f + 1/n \, (\log C_e) \tag{3}$$

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 and thermal modified Udi clay occurred in multi-layer.
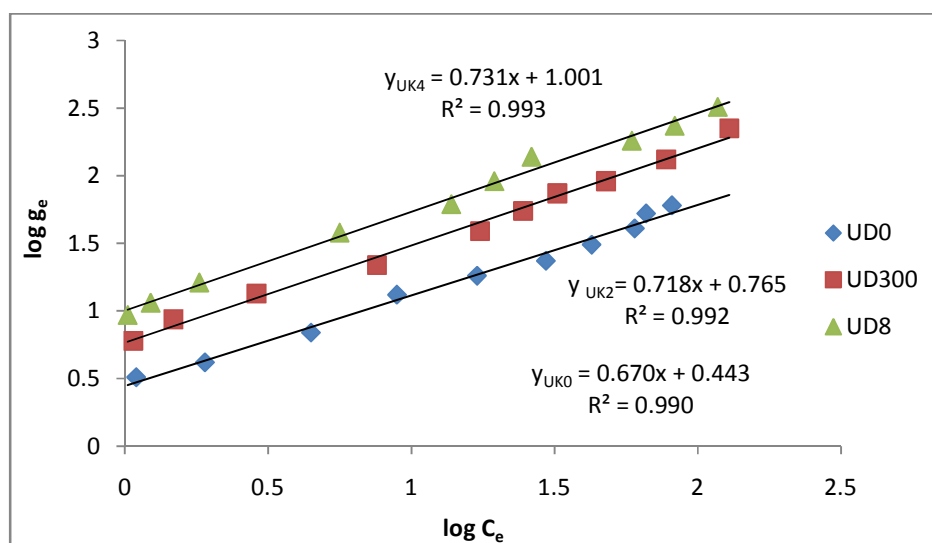

Figure 6: Freundlich adsorption isotherm for colour pigment adsorption onto acid modified Udi clay.

Table 3: 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

CONCLUSION

The modification of the physicochemical properties of Udi clay using thermal and acid activation has been successfully investigated. Results of this work show that acid concentration highly affects the physicochemical properties more than the calcination temperature. The structural change obtained by FTIR analysis indicates that the destruction of the octahedral sheet is a function of acid concentration. The acid activated Udi clay yielded an adsorbent material that is efficient in bleaching off colour pigments from palm oil more than the untreated and thermally activated 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.

2048

_____

REFERENCES

[1] Monvisade P, Siriphannon P, *Appl. Clay Sci,* **2009**, 42, 427.

[2] Chaisena A, Rangsriwatananon K, *Suranaree J. Sci. Technol,* **2004**, 11, 289.

[3] Al-Asheh S, Banat F, Abu-Aitah L, *Sep. Pur. Tech.,* **2003**, 33, 10.

[4] Zorica T, Mladenovic B, Babic M, Logar A, Dordevic R, Cupac B, *J. of Agric. Sci,* **2011**, 56, 25.

[5] Motlagh M, Rigi A, Yuzbashi A, *Int. J. of Engr. Sci,* **2008**, 19, 83.

[6] Motlagh M, Yuzbashi A, Rigi A, *Iranian J. of Mat. Sci. & Engr,* **2011**, 8, 50.

[7] Taha K, Suleiman M, Musa A, *J. of Bangladesh Chem. Soc,* **2011**, 24, 191.

[8] Eze A, Nwadiogbu O, Nwankwere T, *Arch. of Appl. Sci. Research,* **2012**, 4, 792.

[9] Foletto L, Colazzo C, Volzone C, Porto M, *Bra. J. of Chem. Engr,* **2011**, 28, 169.

[10] Wang L, Wang A, *J. Hazard. Mater,* **2008**, 160, 173.

[11] Chen R, Peng F, Su S, *J. Appl. Poly. Sci,* **2008**,108, 2712.

[12] Liu P, *Appl. Clay Sci,* **2007**, 38, 64.

[13] Steudel A, Batenburg F, Fischer R., Weidler G, Emmerich K, *Appl. Clay Sci,* **2009**, 44, 105.

[14] Diaz V, DeSouzaSantozs R, *Quim. Nova,* **2001**, 24, 343.

[15] Doulia R, Leodopoloud C, Gimouhopoulos K, Rigas F, *J. Colloid & Interface Sci,* **2009**, 340, 131.

[16] Lian L, Guo L, Guo C, *J. of Hazard. Mat,* **2009**, 161, 126.

[17] Agalya A, Palanisamy N, Sivakumar P, *Adv. Appl. Sci. Res.*, **2012**, 3 (3), 1220.

[18] Vadivel S, Manickam A, Ponnwsamy S, *Adv. Appl. Sci. Res.*, **2011**, 3(1), 219.

[19] Nwabanne J, Igbokwe P, *Adv. Appl. Sci. Res.,* **2011**, 2(6), 166.

[20] El-Sayed G, Mohammed T, El-Sayed O, *Adv. Appl. Sci. Res.*, **2011**, 2(4), 283.

[21] Nwankwere E, Nwadiogbu J, Yilleng M, Eze K, *Adv. Appl. Sci. Res.*, **2012**, 3(2), 1122.

[22] Tsai T, Hsu S, Su Y, Lin Y, Lin M, Dai H, *J. of Hazard. Mater,* **2007**, 147, 1056.

[23] Korichi S, Elias A, Mefti A, *Appl. Clay Sci,* **2009**, 42, 432.

[24] Mohamedbakr H, Burkitbaev M, *The Open Miner. J,* **2009**, 3, 12.

[25] Temuujin J, Jadambaa T, Burmaa G, Erdenechimeg S, Amaesanaa J, Mackenzie K. D, *Ceram. Intl,* **2004**, 30, 251.

[26] Low K, Lee K, Kong Y, *J. of Chem. Tech. Biotechnol,* **1998**, 72, 67.

[27] Hula N, Onal M, Yuksel S, *Food Chem,* **2007**, 105, 156.