

BLEACHING PERFORMANCE OF A NIGERIAN (YOLA) BENTONITE

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Abstract— The bleaching performance of raw and acid activated Yola montmorillonite clay was studied. The bleaching performance was enhanced upon activation. The predominant active sites on the raw clay are Lewis acid sites, those on the improved clay are Bronsted acid sites. The best bleaching performance was obtained with clay sample activated with 5M H₂SO₄ at acid/clay ratio 0.7, bleaching temperature of 120°C and at 10 minute stirring time. At these conditions the improved clay compares favorably well in terms of bleaching performance with the imported industrial standard sample. Thus, it could be a local substitute for the industrial standard.

Keywords— Bentonite, bleaching, adsorption, β -carotene, palm oil, clay activation.

I. INTRODUCTION

The unique properties of bentonite clay materials had made them valuable in many important industrial applications. These properties include thixotropic, swelling and adsorption. They constitute a peculiar and important group in the field of clay minerals. Application areas include edible oils, fats, industrial oils, soaps, cosmetics, pharmaceuticals, catalysts, paints etc (Takada *et al.*, 1995; Velde 1992; Dear *et al.*, 1989; Ross and Hendericks 1945; Ulrich *et al.*, 1935). This commercial value of bentonite accounted for the large scale mining and exploitations of bentonite deposits at various locations around the globe (Slabaugh and Anne Hiltner 1969; Wander and Haydn, 2004).

In Nigeria, bentonite deposits had been found in different part of the country. An estimated reserve of about 700 million tones had been indicated in the north eastern (black cotton soil) part of Nigeria. These areas comprise of Borno, Yola, Adamawa and Taraba state (RMRDC 1990, 1991; Aribisala 1993). This large bentonite reserve awaits commercial exploration for its various uses, most especially as drilling fluid in the oil industry. However, results from earlier studies revealed that Yola bentonite is a low-grade calcium montmorillonite. It was found unsuitable for drilling fluid applications, even on treatment with sodium salts (James, 2005).

It had been widely reported that acid activated montmorillonite clays have, in particular proved supe-

rior to other clay minerals for removal by adsorption of chlorophyll and other trace pigment from edible oils. And thus remains the principal class of bleaching clay in the oil refining industry (Alexanian 1939; Guillaumin and Pertiniost 1968; Mokoya and Jones, 1993). The acid activation enhances the properties of the montmorillonite by manipulating its physical and chemical properties without destroying its layered crystal structure. Thus the acid activation must be optimized in order to enhance the properties that are responsible for the pigments adsorptions.

It is therefore of interest to establish the best conditions for acid activation of Yola bentonite (acid /clay ratio, acid concentration and the bleaching temperature).

II. MATERIALS AND METHODS

A. Clay activation

Samples of Yola montmorillonite clay were obtained from four locations of the deposit base on nearness to major settlements. The sample lumps were crushed and air dried, grounded and sieved with 150 μ m mesh size. The samples were first treated with H₂SO₄ solution at a chosen concentration of 5M and acid/clay ratio of 0.4. The treatment was carried out as follows: 10 cm³ of 5M H₂SO₄ solution was added to 25g clay sample suspended in 125 cm³ of water. This recipe is equivalent to 20 %($\frac{w}{v}$) clay suspension and 0.4 acid (volume)/clay (mass) ratio. The mixture was maintained at a temperature of 95°C for 3hrs. The resulting mixture was filtered, washed with hot distilled water and air dried. The dried clay was then grounded into fine powder and used to bleach a standard palm oil sample obtained from Global Soap & Detergent Industries, Ilorin.

The effect of variation of the acid/clay ratio on the bleaching performance was examined by varying the volume of the acid solution added in the activation recipe. The acid/clay ratio or acid volume (cm³) examined include: 0.1 (2.5); 0.2 (5.0); 0.3 (7.5); 0.4 (10.0); 0.5 (12.5); 0.7 (17.5); 0.9 (22.5); 1.2 (27.5); 1.5 (37.5) and 2.0 (50.0)

B. Bleaching of palm-oil

The bleaching process was carried out by adding 10g of a sample 100cm³ palm oil at 105°C. The mixture was stirred for a chosen time of time minute, and then filtered to separate the bleached oil from the clay.

The sample with the best performance was used to study the effect of varying stirring time on the bleaching performance.

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The effect of bleaching temperature on the bleaching performance was also studied with the best activated clay sample (AL₈) and its raw (unactivated) sample (UL₈) and an industrial bleaching earth (standard) sample (IS) obtained from Global Soap and Detergent Industries, Ilorin. The temperatures studied include: 60, 80, 100, 120, 140 and 160 °C.

Evaluation of the (UL₈), (AL₈) and (IS) was carried out by varying the mass percent of clay to oil in the bleaching process. The results obtained were evaluated with Freundlich adsorption isotherm.

C. Evaluation of Bleaching Performance

The amount of the colour pigment (carotenoids) was measured in terms of equivalent mg of β-carotene in a unit mass of the oil; this is determined by measuring the absorbance of the oil in cyclohexane at 445nm with UV-Visible spectrophotometer. The expression for calculating equivalent mg of β-carotene in oils according to British Standard Institute (BSI) is as follows:

$$\beta\text{-carotene(mg/kg)} = \frac{383 \times E}{I \times C}$$

where E = Absorbance of the oil in cyclohexane at 445nm

wavelength, C = Concentration of the oil in grams per 100cm³ of solvent (cyclohexane) and I = Path length of the cell used.

The beaching performance was evaluated in terms of % colour pigment removed from a sample after bleaching. This was calculated as follows:

$$\frac{\beta\text{-unbleached oil} - \beta\text{-bleached oil}}{\beta\text{-unbleached oil}} \times 100\%$$

where β = β-carotene.

III. RESULTS AND DISCUSSION

Carotenoids (mainly β-carotene) had been identified as the pigments in palm oil responsible for its red colour. They are soluble in non-polar solvent such as cyclohexane and have common absorption peaks at 444 - 448nm which obeys Beer-Lambert law (Frank, 2002). Bleaching in this context is thus equivalent to removal of colour pigments. Hence, the beaching performance was evaluated in terms of percentage of carotenoids removed from a sample after bleaching. The amount of carotene in the oil before bleaching was 8517.76 mg/kg

Table 1 shows the bleaching performance of the raw and acid activated Yola montmorillonite clay from the four different locations of the deposit. The amount of clay used was 10% ($\frac{w}{v}$) of the oil. The samples were able to remove more than 50 percent of the colour pigment from the oil. The sample L₈ had better bleaching performance than the other three samples. The improvement in the bleaching performance upon acid activation follows a similar pattern as that of the raw samples. It can be said that activation process enhances the clay samples' properties with respect to their applicability as adsorbents. In order to optimize the condition for impacting these desirable properties on the clay activa-

tion parameters acid concentration and acid to clay ratio were varied and their effect on bleaching performance of the samples was studied.

Table 1: Bleaching performance of Yola montmorillonite clay sample from four locations at 0.4 acids (5MH₂SO₄) to clay ratio and at 10% ($\frac{w}{v}$) clay to oil.

Clay sample	% Colour removed	
	Natural Clay	Activated Clay
L ₂	58.80	78.32
L ₅	59.20	83.29
L ₈	64.50	89.74
L ₁₁	59.85	79.63

Table 2 reveals the effect of varying acid/clay ratio on the bleaching performance of the samples. The concentration of acid used is 5M H₂SO₄ at 10% ($\frac{w}{v}$) clay to oil. It shows that the improved performance of about 96% colour removal was obtained at 0.7 acid/clay ratio. Table 3 shows the effect of varying acid concentration on the bleaching performance of the samples. The acid to clay ratio adopted for activation was 0.7 as shown from previous experiment and bleaching carried out at 10% ($\frac{w}{v}$) clay to oil. The result indicated that the percentage colour pigment removed by the samples depends on the level of acid activation.

Table 2: Variation of acid (5M H₂SO₄) to clay with the bleaching performance of the sample at 10% clay to oil

Acid/clay ratio	% colour removed			
	L ₂	L ₅	L ₈	L ₁₁
0.1	52.91	55.54	58.45	51.87
0.2	60.49	62.51	69.29	61.50
0.3	70.60	74.13	75.75	69.70
0.4	77.17	80.03	86.94	79.28
0.5	81.10	84.11	91.97	83.43
0.7	95.52	95.98	96.98	96.46
0.9	91.37	93.52	94.34	91.93
1.2	90.82	91.45	91.25	89.23
1.5	89.19	90.62	89.12	88.90
2.0	87.87	88.88	88.22	87.13

The same pattern was observed for the four samples in both cases, a sharp increase in percentage colour removal from oil with increase level of acid activated was observed. It goes through a maximum of 95% - 97% depending on the location, at acid/clay ratio of 0.7 and 5M H₂SO₄ concentration; after which the bleaching performance gradually decreases with increasing acid treatment. Other workers had reported similar pattern, for example, Mokoya and Jones (1993) obtained acid to clay ratio 0.35 with stocks H₂SO₄ as the optimum condition for the production of acid-activated montmorillonite clay from surrey, South England. An acid/clay ratio of 0.2 and 3M HCl was obtained by Amozie *et al.* (1993) as the optimum condition for producing bleaching clays from some Nigeria kaolinite clay samples.

Contrary to expectation the data in Table 1, 2 & 3 did not agree, this could be due to variation in the particle size of the samples used in the bleaching process. This was not taken into account in this study

Table 3: Effect of acid concentration on bleaching performance of the activated clay samples (activated at acid/clay ratio of 0.7 and at 10% clay/oil)

Concentration of acid (M)	% colour removed			
	L ₂	L ₅	L ₈	L ₁₁
1.0	75.02	75.84	76.08	68.12
3.0	78.44	79.94	80.66	79.02
5.0	94.92	95.64	96.72	95.58
7.0	92.92	93.87	94.85	93.56
8.5	91.89	91.46	91.86	90.4
10.0	87.97	88.02	88.46	89.01

When montmorillonite clays were treated with acid, their chemical composition and physical properties were altered. Properties that had been linked with bleaching performance of montmorillonite clay include surface area, pore volume, and pore size distribution and surface acidity. Mokoya and Jones (1993) demonstrated by infrared spectroscopy of pyridine adsorbed on samples of some raw and acid activated montmorillonite clay, that equilibrium exists between the Lewis and Bronsted acid sites. The Lewis acidity in a montmorillonite arises from isomorphous substitution of Al³⁺ for Si⁴⁺ in the tetrahedral layer of the clay matrix. This provides explanations for the unusually high adsorbent power of bentonites with low SiO₂:Al₂O₃ ratio and high percentage of combined water by Ulrich *et al.* (1935).

In general, acid activation of montmorillonite had been claimed to proceed via original Leaching or the removal of octahedral ions, and any isomorphously substituted tetrahedral ions, and the replacement of the original interlayer or exchangeable cations with hydrogen ions and/or acidic cation (Al³⁺, Fe³⁺, T⁴⁺) from the leach solutions. The protons may occupy positions on the layer matrix thus creating Bronsted acid sites on the clay are not associated with isomorphous, substitution. In addition, the total Bronsted acidity is enhanced by the combined effect of the presence of acidic interlayer cation and less combined with water.

The results in table 4 indicate that, bleaching temperature of 120°C is the optimum bleaching temperature with acid activated montmorillonite AL₈. The industrial sample IS has maximum bleaching performance at 140°C. The optimum bleaching temperature is specific for particular adsorbent and particular oil. However, at temperature greater than 120°C the oil is more prone to thermal/heat bleaching along with adsorption. The thermal bleaching converts the colour pigments into colourless forms. At temperatures above 120°C, the thermal bleaching is accompanied by undesirable structural changes of the oil molecules, most especially unsaturated oil via oxidative degradation, isomerisation and/or polymerisation.

Result summarizes in table 5 also revealed the stirring time of 10 minutes to be adequate for the colour removal process.

According to Proctor and Toro-Vazques (1996), a series of complex interactions controls the adsorption process during vegetable oil refining. The Freundlich adsorption isotherm was originally developed to explain the ad-

sorption of a single solute from solution. However, a similar adsorption pattern had been observed when studying a complex system of adsorption of vegetable oil pigments on bleaching earths. Thus, the Freundlich has been useful in evaluating the commercial value of adsorbents.

Table 4: Effect temperature on the % colour removed

Temperature (°C)	% colour removed			
	Unbleached Oil	Bleached oils with		
		UL ₈	AL ₈	IS
60	0	17.28	44.28	58.96
80	0	25.47	56.59	69.24
100	0.6	30.42	64.12	82.07
120	0.8	47.16	71.57	84.92
140	46.77	48.64	65.52	86.48
160	52.94	24.52	59.29	78.95

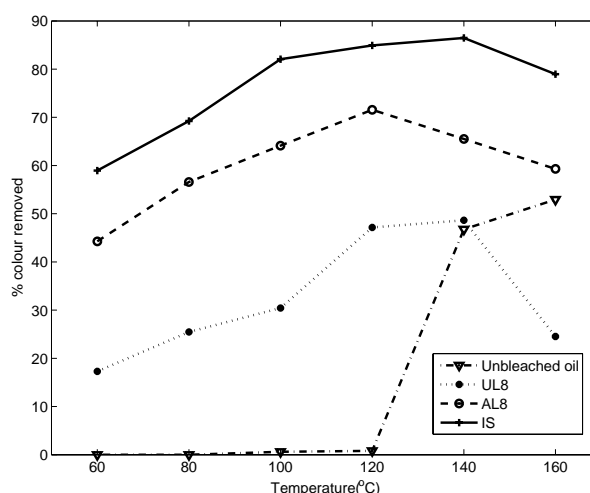


Figure 1: Effect temperature on the % colour removed. Clay to oil ratio 5%; UL₈ unactivated L₈ sample; AL₈ activated L₈ (0.7 acid (5MH₂SO₄)), IS Industrial Sample.

Table 5: Effect of stirring time on bleaching performance of AL₈ Sample at 120°C of 10% clay/oil

Times (minutes)	% Colour removed
2	90.06
4	93.43
6	94.92
8	95.29
10	96.72
12	95.26
14	95.66
16	96.25
18	96.36
20	96.16

From the data in Tables 6, 7 and 8; the Freundlich adsorption isotherm for clay samples UL₈, AL₈ & IS were plotted, the values of 'a' and 'n' were obtained from the graph, where 'a' are the intercepts on the vertical axis and 'n' are the slopes of the graphs. The value of 'a' is a measure of the active surface area of the adsorbent. Unlike Langmuir adsorption model, Freundlich

isotherm is a non-ideal adsorption model, a modification of Langmuir isotherm, which accounts for interaction between adsorbate molecules in both phases. The constant 'n' ($n = \alpha RT$) is related to the energy of interaction between the adsorbate molecules in both phases, where α is a measure of the polarisability of the adsorbate in the bulk oil by those at the surface of the adsorbent

Adsorbent with 'n' values greater than unity, between unity and a half, and less than a half are classified very good, good and poor adsorbent respectively. The value of 'n' is also a measure of the number of layers of the colour pigment adsorbed per active site of the clay and can give indication of the kind of forces causing the adsorption process.

In physisorption, the electron cloud of the substance adsorbed interacts as a whole with the adsorbent, the adsorbent could only effect polarisation of the adsorbate. In chemisorptions, electron transfer or sharing of electron (formation of new molecular orbital) do take place between the adsorbate and adsorbents as in the case of normal chemical compound. Different thermal effects accompany the two types of adsorption. There are two kinds of adsorption site on the clays samples, Lewis acid sites and Bronsted acid sites causing physisorption and chemisorption respectively. Acid activation drastically reduces the Lewis acid sites but generate Bronsted acid sites on the clay matrix. This accounts for the observed change in the values of parameter 'a' and

'n' for UL_8 adsorption in UL_8 is predominantly by physisorption, while adsorption in AL_8 and IS is accompanied by dark blue colouration similar to Carr Price reaction. This suggests that the mechanism of adsorption in AL_8 and IS is similar and equally indicates that IS is an acid activated clay. The values of 'a' and 'n' of clay samples UL_8 , AL_8 and IS are summarized in table 9. The result revealed that sample AL_8 compares favourably with sample IS.

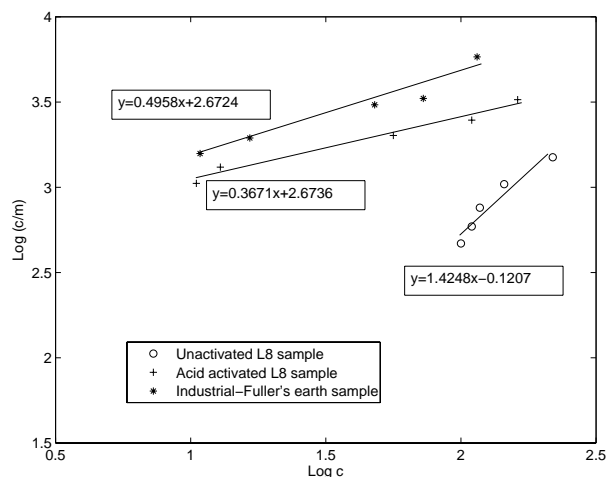


Figure 2: Effect of variation of amount of selected clay samples on their bleaching performance

Table 6: Effect of variation of amount clay (UL_8) on its bleaching performance

Mass (m)	% Clay/oil	β -Carotene in oil after bleaching mg/kg (c)	β -Carotene removed mg/kg (x)	% Carotene removed	log (x/m)	log c
0.125	5	217.97	187.63	46.26	3.176	2.34
0.250	10	145.20	260.39	64.20	3.018	2.16
0.375	15	119.85	285.75	70.45	2.880	2.07
0.500	20	108.86	296.75	73.16	2.770	2.04
0.625	25	100.55	305.05	75.16	2.670	2.00

Table 7: Effect of variation of amount of clay (AL_8) on its bleaching

Mass (m)	% Clay/oil	β -Carotene in oil after bleaching mg/kg (c)	β -Carotene removed mg/kg (x)	% Carotene removed	log (x/m)	log c
0.075	3	160.54	245.05	60.42	3.514	2.210
0.150	6	109.67	295.93	72.96	3.394	2.040
0.225	9	56.05	3.44.55	86.18	3.304	1.750
0.300	12	12.90	393.31	96.97	3.118	1.110
0.375	15	10.50	395.10	97.11	3.023	1.021

Table 8: Effect of variation of amount of clay IS on its bleaching performance

Mass (m)	% Clay/oil	β -carotene in oil after bleaching mg/kg (c)	B-carotene removed mg/kg (x)	% Carotene remove	log (x/m)	log c
0.05	2	114.33	290.77	71.67	3.765	2.060
0.10	4	73.7	331.90	81.23	3.521	1.861
0.15	6	42.5	236.87	89.47	3.484	1.681
0.20	8	16.55	389.05	95.92	3.289	1.219
0.25	10	10.83	394.77	97.33	3.198	1.035

Table 9: characteristic parameter of the bleaching clay sample

	Parameter	
	a	n
UL ₈	0.757356	1.4248
AL ₈	471.6285	0.3671
IS	470.3271	0.4958

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