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Performance Evaluation of Acid Treated Clays for Palm Oil Bleaching

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Abstract: Palm oil bleaching using acid treated clay was investigated. Colorimeter was used to determine the colour in form of absorbance for the crude and refined palm oil. These were used to determine the percentage colour reduction. Effects of acid type, acid concentration and mass of adsorbent using Freudlich adsorption isotherms were studied. Results of the investigation revealed that HCl activated clay has relatively higher bleaching power than H_2SO_4 activated clay. The increase in acid concentration increases bleaching efficiency. The maximum percentage colour reduction of 94.28% was achieved in HCl activated clay at 45% acid concentration, while 89.46% colour reduction at 35% acid concentration was achieved with H_2SO_4 activated clay. Further increase in concentration of H_2SO_4 has no significant effect. The Freudlich adsorption constant n and k values for various clay samples showed that sample E has the highest bleaching power with 94.28% colour reduction, followed by sample A with 85.00% and sample B with 84.82%, samples C and D are not very effective in the activated state.

Key words: Adsorption, bleaching, absorption, palm oil, clay, Freudlich

INTRODUCTION

Palm oil is widely used for cooking and for making soap throughout the world. Other non-edible uses include manufacture of grease, lubricants, candles and paints. It is physically refined without the use of chemical solvents, thereby reducing the risk of contamination. In oleo chemical industries, Refined, Bleached and Deodorized (RBD) palm oil are used and the bleaching aspect is best performed by adsorption process using adsorbent.

The removal of pigment and other various trace constituents by adsorption process is one of the most important steps in the vegetable oil refinery and this process removes the colour bodies, which include carotenes, chlorophyll and other pigments as impurities 9. The process renders the oil or the product from the oil more appealing and convenient for use. Bentonite or activated clay has been widely employed as an adsorbent. In recent years, Nigerian clay has been found competent in the adsorption bleaching of palm oil.

The mechanisms for adsorption in oil bleaching industry are different and diverse. Proctor and Palaniappan (1989) found that the adsorption of luxein from soy/hexane miscella on rice hull ash was a physical process while that on activated clay was a chemical one. On the other hand, Liew *et al.* (1993) claimed that the removal of carotene from palm oil/hexane miscella by activated rice hull was due to chemisorptions.

While the bleaching power of clay is very high, efforts have been made to promote the efficiency of Nigeria clays by varying the acid involved. Numerous researches have been carried out on clay activation and bleaching of vegetable oil using activated and non-activated Nigeria clays. Clay in the old Bendel state now Edo and Delta states were used both in crude state and activated state to bleach palm oil with a percentage colour reduction above 90% (Hymore and Iyoyi, 1989). Ukpor clay from Enugu state was used by Okeke (1990) for the adsorption bleaching of sheanut oil at 140°C bleaching temperature with well over 80% colour reduction achieved. Moreover, the study of activated bleaching power of some selected Nigerian clays which include clays found in Shagamu and Ewekoro, both in Ogun state; Calabar in Cross River state and Nsukka, Enugu state, with a view to initiating the utilization for bleaching earth manufacture was carried out by Oboh *et al.* (1987) and reasonable percentage colour reduction around 80% was achieved.

Studies carried out so far on the previous research work shows that much has not been carried out on the clays found in the northern and western part of the country. Therefore, the objective of this study is to evaluate the effectiveness of the clays found around Oyo and Osun States of Nigeria with a view to comparing their adsorptive power to the clays found in the other part of the country.

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MATERIALS AND METHODS

Clay samples A, B and E were obtained locally from Ogbomoso and Ibadan (Oyo State) while clay samples C and D were obtained from Ejigbo and Osogbo (Osun State) respectively. The Crude Palm Oil (CPO) was obtained locally from Ogbomoso market. Sulphuric and Hydrochloric acid used for acid activation were analytical grade manufactured by Fisons Plc England.

Acid activation of clay samples: A thermostatically controlled water bath maintained at 100°C was used. Slurry of the purified clay sample was made with distilled water in a 500 mL beaker. Activation was carried out by adding the acid of a known concentration to the clay slurry and the mixture boiled for 2 h in the water bath maintained at 100°C. After 2 h, the slurry was poured through a bunchner funnel to separate clay and acid. The filtered clay was washed with distilled water several times at room temperature removing the residual acid in the process. The washed clay was then dried in an oven until the weight of the clay remained constant. HCl and H_2SO_4 with varying concentrations of 15, 25, 35 and 45% were used in the activation process.

Bleaching of palm oil: Thirty gram of degummed, neutralized and dried oil and 1.5 g of activated clay were charged into a beaker (250 mL) and heated at constant temperature of 100°C for 5 min in a water bath. The slurry in the beaker was agitated by a stirrer. The slurry was filtered through a dry filter paper after the predetermined adsorption time. Filtered oil was then collected for analysis.

Adsorption isotherms: The adsorption bleaching process described above was carried out. The mass of clay was varied between 3 and 10% mass of the oil. Selected mass of clay sample was used to bleach 30 g of oil sample. The experimental results were subjected to Freudlich adsorption equation given below:

$$\text{Log } x/m = \log k + n \log c \quad (1)$$

Where:

x = The amount of substance adsorbed
m = The amount of adsorbent
c = Concentration of the residual substance
k and n = Adsorption isotherms constants.

x, m and c as shown in Eq. 2 were evaluated and the values obtained were used in the log log plot of x/m versus c for the evaluation of n (the slope) and k (the intercept) of the graph. The same procedure was used for all the clay samples.

Determination of percentage colour reduction [%CR]: The absorbance of palm oils before and after bleaching was measured by Griffin colorimeter. By comparing the absorbance of the bleached oils with the crude palm oil, the percentage colour reduction was evaluated using the equation bellow:

$$\% \text{ CR} = (Ab_0 - Ab_x)/ Ab_0 * 100 \quad (2)$$

Where:

% CR = Percentage colour reduction (%)
Ab_0 = Absorbance of the crude palm oil
Ab_x = Absorbance of the bleached palm oil

Clay characterization: The percentage composition of inorganic compound like Al_2O_3, SiO_2, Fe_2O_3, MgO and CaO were determined using gravimetary and colorimetry method.

RESULTS AND DISCUSSION

Effect of acids on clay activation: All the clay samples were activated with HCl and H_2SO_4. Bleaching efficiencies measured in terms of percentage colour reductions are shown in Fig. 1 and 2 where acid concentration was plotted against %CR. Figure 1 and 2 shows that clay activated with HCl has greater efficiency than that activated with H_2SO_4. Maximum %CR of 94.20 was achieved in clay E when HCl was used whereas 89.46% maximum %CR was achieved when H_2SO_4 was used. This is traceable to the high solubility of the chlorides of Mg, Ca and Fe than that of the sulphates of the same metals. Proctinor and Palaniappan (1989) and Brace (1973) attributed the high adsorptive power of HCl activated clays to the complete removal of aluminium, magnesium and calcium ions within the crystal of the clay. Based on these explanations, It may be inferred that impurities such as Fe_2O_3, CaO and MgO etc. that cover part of the active sites are washed away by acid activation and number of active site available for adsorption increased.

Effect of concentration variation on the activation: In the experiments performed with various concentrations of acid, bleaching efficiency increased with increase in acid concentration (Fig. 1 and 2). Thirty five percent was found to be optimal concentration in clay sample A, B, C and D while 45% concentration was optimal for clay sample E

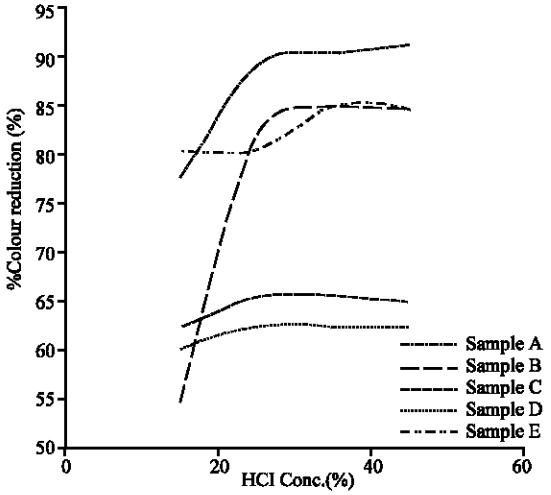

Fig. 1: Graph of % colour reduction vs. HCl Conc

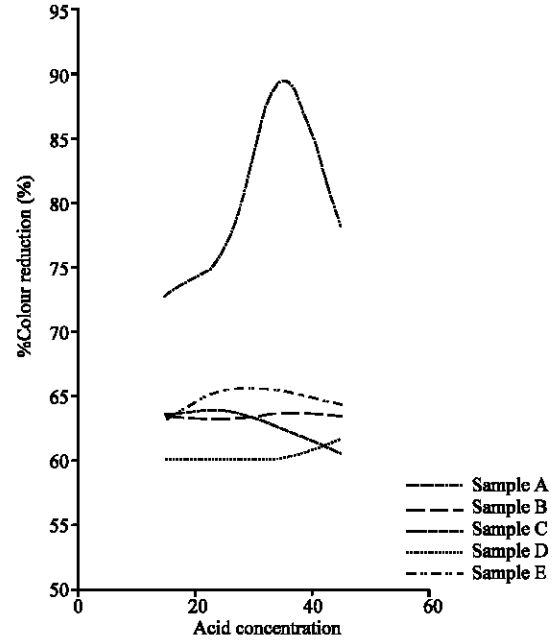

Fig. 2: Graph of % colour reduction vs. H_2SO_4 Conc

when Hcl was used for activation. However, when H_2SO_4 was used, the optimal concentration was found to be 25% for clay samples A and C, 35% for clay samples B and E and 45% for clay sample D. These irregularities in optimal concentration values could be traced to the mineralogical composition of each of the clay sample (Table 1) and their geographical location as stated earlier. The same trend was also observed by Chiang *et al.* (1996).

Effect of mass of adsorbent (Adsorption Isotherms): The effectiveness of the clay samples was further investigated

Table 1: The average value for mineralogy test

Clay sample	CaO %	MgO %	Fe_2O_3 %	Al_2O_3 %	SiO_2 %
A	0.00±0.00	0.03±0.01	3.30±0.00	5.22±0.00	90.36±0.01
B	0.00±0.00	0.02±0.00	3.13±0.01	6.22±0.01	90.09±0.01
C	0.00±0.00	0.06±0.01	3.12±0.01	8.04±0.03	80.22±0.03
D	0.00±0.00	0.01±0.00	10.80±0.01	6.51±0.01	81.89±0.01
E	0.02±0.00	0.30±0.01	2.52±0.01	5.18±0.03	91.29±0.01

Table 2: % CR, n and k values from the isotherms plot for local activated clay samples and Imported Bleaching Earth (IBE)

Adsorbents	%CR	n	k
Clay sample A	65	3.86	0.28
Clay sample B	64.82	3.90	0.37
Clay sample C	45.53	4.70	0.55
Clay sample D	42.51	*	*
Clay sample E	74.28	3.60	0.14
IBE	80.00	3.30	0.14

* Low adsorptive power and least effective clay

using the concept of Freudlich adsorption isotherms. Freudlich equation is valid for any method of colour measurement, as long as the units of measurement are additives and proportional to the actual concentration of colouring materials in the oil (Hui, 1996). The values of n and k (Freudlich adsorption constant) calculated, using Eq. 2 show that clay sample E is mostly effective followed by clay samples A, B and finally C (Table 2). This could be attributed to the fact that the value of n determines the degree of decolourization within which the adsorbent exhibit its greatest relative effect. If n is high, the adsorbent is relatively inefficient as an agent for effecting a high degree of decolorization while if n is low, the reverse is the case (Okeke, 1990). Furthermore, from practical stand point, k-value is a general measure of the activity of the adsorbent hence, high values of k does not mean high or low efficiency, it only shows the rate of adsorption in each clay, whereas n is an indication of its characteristics manner of adsorption (Hui, 1996). n and k-value could not be determined for clay sample D and this could be traced to its low adsorptive power, hence, it is considered the least effective.

CONCLUSION

- Acid activation increases the bleaching power of Nigerian clays and generally hydrochloric acid activated clays proved more effective than sulphuric acid (HCL > H_2SO_4).
- Bleaching efficiency of acid treated clay increases with concentration.
- Optimal concentration is found between 35% and 45%.
- The dose of Nigerian clays required for palm oil bleaching ranges between 5-10% mass of the oil.

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