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# Kinetic investigation of the adsorptive removal of B-carotene pigments from palm oil using unmodified natural clay

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# ABSTRACT

Kinetic studies on the adsorption of  $\beta$ -carotene from palm oil on local bentonite clay (Ukpo Clay) have been investigated. This study demonstrates that the clay is efficient in the adsorption of  $\beta$ -carotene and free fatty acids from edible oils. The bleaching efficiency has been determined with the aid of a colorimeter. The rate constant obtained from the zeroth order kinetic equation was  $0.002 \text{min}^{-1}$ . The manner of adsorption of palm oil on the clay was chemisorption and the  $\Delta G^{\dagger}$  of the system obtained was  $112.66 \text{KJmol}^{-1}$  using the absolute rate equation. This study lead to the conclusion that the local clay is a very potent adsorbents for bleaching vegetable oils.

Keywords: Adsorptive purification, bleaching, ukpo clay, Kinetics,  $\beta$ -carotene.

## INTRODUCTION

Various naturally occurring clays have found significance for adsorptive purification. Adsorptive purification, in its most general sense, involves the use of adsorbents to remove undesirable constituents and contaminants from fats and oils by adsorptive mechanisms [1]. A very important aspect in the field of clay minerals is its use in bleaching of vegetable fats and oils to improve its nature. Various studies have also been carried out, with or without modification, in the use of clays to purify edible oils by adsorption [2], [3], [4], [5]. Palm oil is a special kind of vegetable fats and has found extensive use for domestic and industrial purposes [4]. Crude palm oil contains about 500 to 700mg/kg of carotenoids and 600-1000mg/kg of tocopherols [6]. Carotenoids (mainly  $\beta$ -carotene) have been identified as the pigment in palm oil responsible for its red color and have adsorption peaks of 444-490 [4]. Palm oil is generally refined by adsorptive purification that involves degumming, bleaching and deacidification [3], [4], [7]. Low grade bentonite from Ukpo, Nigeria, has been selected for investigation, without modification, of its capacity to bleach palm oil. The authors have studied the kinetics of the adsorptive purification of crude palm oil using these clays to explain how  $\beta$ -carotene pigments are transported out of the oil with time and the manner of adsorption on the clay.

# MATERIALS AND METHODS

Palm oil was obtained from a local store within Enugu metropolis. Ukpo clay used as adsorbents was obtained from Ukpo, Anambra State Nigeria. All Reagents used were analytical grade reagents. All glassware were washed thoroughly and carefully rinsed in 0.5% Nitric acid solution then kept to dry in an oven at  $105^{\circ}$ C.

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#### 2.1 Preparation of the Bleaching Adsorbent

Ukpo Clay was grinded to powder using a laboratory mortar and pestle. The powdered clay were washed with distilled water to remove any surface impurities and kept in an oven to dry at 105°C for 24hrs before crushing to powder and stored for further used.

#### 2.2 Procedure for adsorptive purification

An Amount (20g) of Palm oil was measured into a 100ml beaker. To the oil in the beaker, 2g of phosphoric acid was added and the mixture kept in a thermostated water bath set at 99.9°C for about 30 minutes to set the oil for bleaching. After 30 minutes, 5g of the adsorbent was carefully added into the mixture and stirred at intervals for 15minutes to achieve complete mixing between the Oil, phosphoric acid and the adsorbent. After 15 minutes, the slurry was filtered with Whatman filter paper into a test tube. The colour of the oil was tested using a photocolorimeter at 490nm. The experiments were subsequently repeated at 30, 60, 90, 120 and 150 minutes to test the effect of time on the adsorptive purification of palm oil. The Acid Values were subsequently tested after each experiment using the methods of Van Eys et al. [8] and thus the free fatty (palmitic) acid content.

2.3 Colorimetric Determination of bleaching Extent: An Avis photocolorimeter (Model 312) was used to determine the absorbance of the oil samples at 490nm. Prior to each reading, the samples were mixed with hexane (10% oil in hexane). The extent of bleaching was presented as %Reduction in absorbance of purified oil relative to initial absorbance crude palm oil sample in hexane. The extent of bleaching was calculated thus:

Extent of  $Bleaching(\%) = 100 - \frac{Absorbance of bleached Sample}{Initial Absorbance of crude Sample} \times 100$ 

## **RESULTS AND DISCUSSION**

S/N	Time(Minutes)	Absorbance	% Bleaching	FFA (%)
0	0	0.61	0	39.5
1	15	0.58	4.92	14.3
2	30	0.50	18.03	10.7
3	60	0.45	26.23	6.7
4	90	0.38	37.70	6.4
5	120	0.29	52.46	6.4
6	150	0.20	67.21	6.5

# **Effect of Time of oil Absorbance**



Figure 1: Effect of bleaching time on the Absorbance of palm oil.

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**Effect of Time on Bleaching** 

The Adsorptive purification of the palm oil was carried out at a thermodynamic temperature of 373K in a thermostated water bath. Adsorptive purification in this context is the bleaching or reduction of carotenoids in the oil sample. Hence adsorptive purification performance of the clay on the oil sample was determined in terms of bleaching efficiency, using a colorimeter, after the purification procedure. The properties of the purified oil after each experiment are shown in table and the bleaching efficiency rate is illustrated in Figure 2. The removal of pigment from the oil without modification of the clay was successful. This is in contrast with the idea that acid activation must first be carried out in order to enforce bleaching or to enhance the property of the clay that are responsible for pigment adsorption. This is attributes to strong interactions between the clays and adsorbate surface

during the procedure [13]. Time effect is also reflected in the change in acid value and free fatty acids. The results have shown that free fatty acids of the oil reduce as purification time increases. The result of the FFA confirms the findings of Nde-Aga et al. [4] and demonstrating that palmitic are also adsorbed on the clays and peroxides are destroyed during the process. This is in diametric contrast with the findings of other researchers [9], [10] [11] whose results show that the acid value increases during discoloration of the oil. This could have been as a result of the adsorbent used, the nature of modification, the kind of catalyst used or the method with which the experiments where performed.

### **3.1 Kinetics of Bleaching**

The effect of time on the absorbance and extent of bleaching of palm oil are reflected in Tables 1 and 2 respectively. The data were tested with the several kinetic models in order to describe the adsorptive interaction between the  $\beta$ carotene and the Ukpo clay used. With an  $R^2$  value of 0.991, the experimental data fitted most appropriately into the 0<sup>th</sup> order rate equation

$$r = -\frac{\delta[C]}{\delta t} = k[C]^n$$

[ Also expressed as

$$C] = [C]_0 - kt$$

C is the concentration of sample, t is the time of purification, k is extraction coefficient and n represents the order of reaction (in this case n = 0). Since absorbance is directly proportional to concentration and the molar absorbance is constant (Beer-Lambert Law), the values of the absorbance were plotted against the time of reaction. The linear plot of Absorbance against concentration is a straight line (Table 1) whose slope is equal to k. Figure 1 also illustrates the kinetics of carotenoids adsorption onto clay. The value of  $r = k = 0.002 \text{ min}^{-1}$  (for 0<sup>th</sup> Order). The rate of adsorption of  $\beta$ -carotene from the oil mass can therefore be said to be a single step mechanism, in agreement with the findings of [2] in their study of the mechanism of adsorption of  $\beta$ -carotene on acid activated clay using infrared and ultraviolet spec with adsorption techniques. This demonstrates that the reaction is independent of the concentration of  $\beta$ -carotene in the palm oil and that the speed of reaction increases with a constant increase in time. It is assumed

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that the main kinetic process is the motion of the pigment in the oil to vacant site near it (the clay surface). That is to say at a lesser time, there is less transport of  $\beta$ -carotene from the oil to the clay. To further investigate the energy behavior and the manner of transport of the pigment from the oil mass,  $\Delta G^{\neq}$  value was calculated from the experimental rate constant *k* via the conventional form of the absolute rate equation:

$$\Delta G^{\neq} = RT[\ln(K_B/h) - \ln(k/T)]$$

Where k represents the reaction rate,  $K_B$  is the Boltzmann constant, T the thermodynamic temperature and  $\Delta G^{\ddagger}$  is the free energy of transportation and h the Planck constant ( $K_B/h = 2.08358 \times 10^{10} \text{ K}^{-1} \text{ s}^{-1}$ ). The values of the rate constants, and hence Gibbs energies of activation, depend upon the choice of concentration units (or of the thermodynamic standard state). The results of the experiment were fitted directly into the equation to obtain an estimation of  $\Delta G^{\ddagger}$  in the system. The value of  $\Delta G^{\ddagger}$  obtained is 112.66KJ/mol. The value indicates that the reaction is not spontaneous and that the manner of adsorption is chemisorption. This corresponds with the results of [12] in the adsorption of carotene from maize oil. In chemisorption, molecules form covalent bonds with the clay surface. The adsorption process is primarily dictated by the interaction between these surface species and the  $\beta$ -carotene molecules. Depending on the energy barrier involved, an organic molecule may undergo bond breaking or bond-making to form a covalent bond with the adsorbent surface [1].

# CONCLUSION

The kinetic study of the adsorptive purification of palm oil using Ukpo clay without modification has been demonstrated. The adsorption of pigments onto clay surface with increase in time were shown to be independent of the concentration of the pigment in the oil. The removal of pigments can also be correlated to the degree of free fatty (palmitic) acid in the oil. This implies that the purification procedure not only makes it possible to give an attractive color to the palm oil but also produces a stable oil of good quality. The rate of the bleaching was recorded to be 0.44%/min and the rate of reaction was  $0.002 \text{min}^{-1}$  change in Absorbance. The value of  $\Delta G^{\dagger}$  (112.66KJ/mol) shows that the entire process is a chemical reaction and thereby not spontaneous. The results of this study clearly indicates that Ukpo clay is clearly a good adsorbent for the purification of palm oil and thus a recommended local substitute for industrial application and further research.

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