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# A Study of the Adsorptive and Oxidative Bleaching of Palm Oil Using Clay and Potassium Tetraoxomanganate V11 Materials

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**Abstract**

Fats and oils undergo hydrolysis reaction. They hydrolyse to yield propane-1,2,3 triol and the corresponding alkanoic acids if it is acid hydrolysis. Alkaline hydrolysis yields sodium or potassium salt of the alkanoic acid and propane-1,2,3-triol. A common approach for bleaching palm oil has been the use of clay materials, particularly the commercially available fuller's earth. In this study, the suitability of chemical bleaching of palm oil using acidified (0.1M $H_2SO_4$) and non-acidified 1.0M $KMnO_4$ was examined. This is compared to the adsorptive procedure using clay materials. Average bleaching absorbance values of $0.017\underline{+}0.005$ and $0.115\underline{+}0.004$ for acidified and non-acidified $KMnO_4$ were respectively obtained from the oxidative bleaching procedure. Those for fuller's earth and its blend with sodium sesquicarbonate (trona, a locally obtained clay) gave absorbance values of $0.121\underline{+}0.011$ and $0.186\underline{+}0.006$ respectively; while that for trona/activated carbon blend was $0.234\underline{+}0.007$. These are in comparison to 0.881 for the unbleached palm oil. Thus, a relatively better bleaching was achieved with the oxidative process. A first order rate reaction with respect to the bleaching agents was obtained for both procedures. Rate constants of $0.079\underline{+}014$ (acidified) and $0.055\underline{+}0.020 min^{-1}$ (non-acidified) at $80^0C$ were recorded for the oxidative bleaching. These are compared to $0.034\underline{+}0.009$ obtained for the clay mixture. Half-life values of 10min for acidified oxidative process, and 28min for adsorptive clay mixture method, were obtained. Efficiency of 98% was obtained for the acidified oxidative compared to approximately 70% for the clay blend. A significance, $p\underline{<}\ 0.05$, between the absorbance values for the acidified oxidative and each of the adsorptive clay bleaching procedures was obtained.These observations indicate the potentials of oxidizing agents especially the acidified $KMnO_4$ in the bleaching of palm oil, and therefore, suggest its usage industrially for this purpose.

**Keywords:** palm oil, adsorptive, oxidative, bleaching, clay and $KMnO_4$ materials

## 1. Introduction

Fats and oils are mixtures of various alkanoates (esters) formed by the union of three molecules of long carbon-chain alkanoic acids (fatty acids or carboxylic acids) with one molecule of a trihydric alkanol called propane-1,2,3-triol (glycerol) (Philip Matthews, 2004).

Palm oil is formed by the reaction of hexadeconoic acid (palmitic acid) and ethylhydroxide ($CH_2OH$) producing a pamitate (Philip Matthews, 2004), represented as below:

$3C_{15}H_{31}COOH$

|

$CHOH$ $+ CH_2OH \longrightarrow 3\ C_{15}H_{31}COOH_2 + 3H_2O$

|

$CH_2OH$ ethylhydroxide $C_{15}H_{31}COOH$

Hexadecanoic Acid $C_{15}H_{31}COOH_2$

(palmitic acid) Palmitate

Bleaching of palm oil serve as a means of enhancing its industrial utilization. Adsorptive bleaching process utilizing clays particularly the commercially available Fuller's earth and locally obtained sodium sesquicarbonate (trona), and activacted carbon has been a common process (Gregg and Sing, 1967). Odoemelam (Odoemelam,1998) examined the use of several locally sourced clay materials in the bleaching of palm oil.

This study seeks to investigate the oxidative process using acidified and non-acidified $KMnO_4$ as the oxidants as has been reported (Ogugbuaja and Akpomie, 2003) in comparison to the commonly used fuller's earth, and 40:60 mixture ratio of Fuller's earth to trona. The oxidative potential of acidified $KMnO_4$ is well known and has been utilized in several oxidizing processes. The amenability of this oxidative procedure, which might be of industrial application, is of research interest.

## 2. Materials and Methods

### *2.1 Materials Used and Their Sources*

Raw palm oil sample and trona (sodum sesquicarbonate) were obtained from uruekwo village, Enugu-Ukwu in Anambra State. Activated carbon (made in Thailand) and Fuller's earth (Fulmont type A) were obtained from Godwin-Kris rubber industries, Nnewi Anambra State, Nigeria. The materials were kept in a refrigerator until when needed.

### *2.2 Extraction Method and Analytical Procedure*

#### 2.2.1 Palm Oil Sample Purification and λmax Determination

Some quantity of the palm oil was filtered by suction. A portion of the filtrate, 0.1ml, was diluted with 20ml cyclohexane as has earlier been reported according to (Ogugbuaja and Akpomie, 2003). The maximum wavelength, λmax, was determined as 460nm using GENWAY 6300 UV spectrophotometer. The pH of the palm oil was obtained as 4.6 using standard procedure (Ogugbuaja, 2000).

#### 2.2.2 Bleaching of Palm Oil

In a typical palm oil bleaching by clay adsorption process, 5g each, of fuller's earth, 60:40 (3g to 2g portions) of trona to fuller's earth ratio and trona to activated carbon were used. In case of the oxidative bleaching process, 20ml 1.0M $KMnO_4$ acidified with 1.0ml 0.1M $H_2SO_4$ and non-acidified $KMnO_4$ were used. For the bleaching process, 50g aliquots of filtered fresh palm oil samples were added to each of the bleaching agents. The mixtures were placed in a water bath thermostated at $80^0$C and stirred continuously for 60min and then left to cool. After cooling, and filtering by suction, their absorbance values were determined. Replicates of all these were carried out and the average absorbance values of each recorded as a function of time. The absorbance of the unbleached palm oil was determined as 0.881.

### *2.3 Kinetics Study*

The order of reaction, and rate constants of the bleaching processes were determined at 60min and $80^0$C by using appropriate formula and graphical evaluation procedure as reported in (J.O. Nwadiogbu et all, (2014).

## 3. Results

The result obtained in this research were presented in tables 1, 2 and 3 below:

Table 1. Absorbance values of bleaching 50g 0f palm oil using bleaching agent of potassium tetraoxomanganate ($KMnO_4$) vii

| S/N | Sample | | Bleaching Agent | |
|---|---|---|---|---|
| | Fullers earth | Fullers earth/Trona 40:60 | 1.0M KMnO4 Acidified | Non acidified |
| 1 | 0.116 | 0.181 | 0.014 | 0.112 |
| 2 | 0.114 | 0.184 | 0.018 | 0.116 |
| 3 | 0.116 | 0.194 | 0.024 | 0.114 |
| 4 | 0.138 | 0.186 | 0.014 | 0.121 |
| 5 | _ | _ | 0.013 | 0.110 |
| Mean | 0.121+0.011a | 0.186+0.006b | 0.017+0.005c | 0.115+0.004a |

❖ Mean values with different letters are statistically different at 95% confidence level.

Table 2. Absorbance Values of bleaching 50g of Palm Oil using Bleaching agent of Trona/Activated carbon

| S/N | Sample | | Bleaching Agent |
|---|---|---|---|
| | Fullers earth | Fullers earth/Trona 40:60 | Trona/Activated carbon |
| 1 | 0.116 | 0.181 | 0.242 |
| 2 | 0.114 | 0.184 | 0.228 |
| 3 | 0.116 | 0.194 | 0.236 |
| 4 | 0.138 | 0.186 | 0.226 |
| 5 | _ | _ | _ |
| Mean | 0.121+0.01 1a | 0.186+0.00 6b | 0.234+0.00 7d |

- **Mean values with different letters are statistically different at 95% confidence level.**

Table 3. Kinetics studies absorbance values and rate constants data, of bleaching of 50g palm oil at 80oC using clays (adsorptive) and KMno4 (oxidative) bleaching agents

| Time (min) | Bleaching agents A | | B | | C | |
|---|---|---|---|---|---|---|
| | $Ab_A$ | $K_A$ | $Ab_B$ | $K_B$ | $Ab_c$ | $K_C$ |
| 10 | 0.601 | 0.051 | - | - | - | - |
| 20 | 0.512 | 0.030 | 0.174 | 0.086 | 0.125 | 0.104 |
| 30 | 0.334 | 0.036 | 0.155 | 0.062 | 0.106 | 0.075 |
| 40 | 0.302 | 0.030 | 0.131 | 0.051 | 0.048 | 0.076 |
| 50 | 0.261 | 0.027 | 0.129 | 0.041 | 0.030 | 0.070 |
| 60 | 0.181 | 0.028 | 0.112 | 0.036 | 0.014 | 0.071 |
| Mean | 0.034±0.009 | | 0.055±0.020 | | 0.079±0.014 | |

**Key**: A= 60:40 ratio of trona: fullers earth; B=non acidified and C=acidified KMnO4 K= the respective rate constants (min-1); Ab =absorbance.

From the table of result in 1, 2 and 3, the plots of log A versus time were plotted and shown in graphs as figures 1-3 as follows:

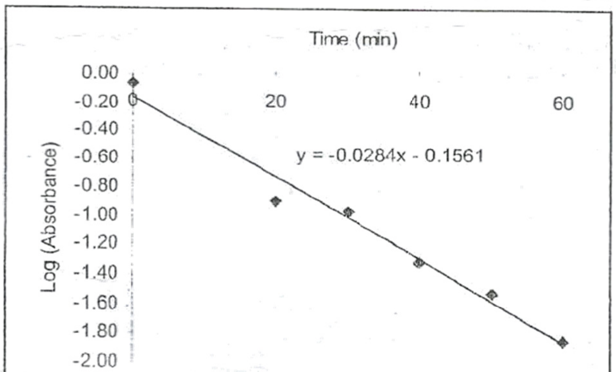


Figure 1: Plot of log (Absorbance) against time for acidified oxidative bleaching of palm oil by $KMnO_4$ at 80°C

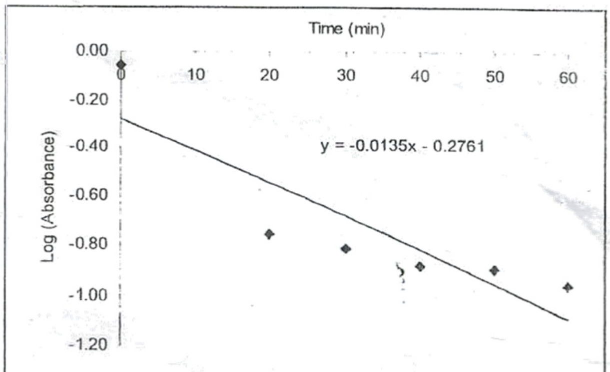


Figure 2: Plot of log (Absorbance) against time for non-acidified oxidative bleaching of palm oil by $KMnO_4$ at 80°C

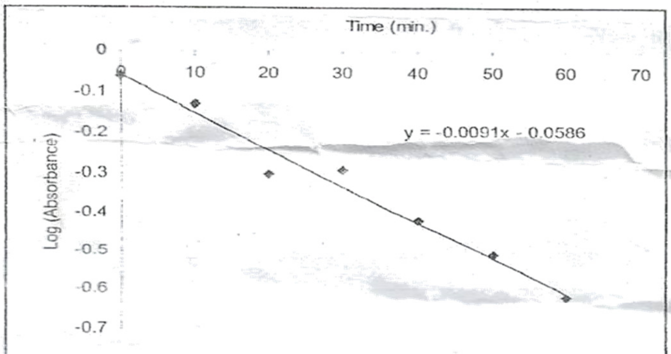


Figure3: Plot of log (Absorbance) against time for bleaching of palm oil using Trona-Activated Carbon blend at 80°C

## 4. Discussion

Mean absorbance values for the four bleaching agents used are presented in table 1, respective values of 0.121$\pm$0.011, 0.186$\pm$0.006, 0.017$\pm$0.005 and 0.151$\pm$0.004 were recorded for the fuller's earth, trona:/fuller's earth blend, the acidified and non-acidified oxidation processes using KMnO4. The bleaching agent of trona/activated carbon in table 2 also recorded, and the mean absorbance value of 0.234±0.007 was obtained.

In table 1, it is evident that more efficient bleaching was obtained from the use of acidified KMnO4; up to 98% bleaching efficiency was obtained from this oxidative procedure. This is as compared to 86% for Fuller's earth and about 70% for the trona blends. Statistically, there was a significant difference ($p \leq 0.05$) between the results for the acidified oxidation and the other processes. However, no statistical difference existed between the results for the fuller's earth and the non-acidified $KMnO_4$ bleaching processes at $p \leq 0.05$.

The adsorptive bleaching process by clay materials is a surface phenomenon according to J.O. Nwadiogbu et,al, (2015) This is noted to be dependent on the apparent bulk density (ABD), the moisture content,

particle size, loss on ignition, and acidity of the oil. These characteristics collectively play some roles in the bleaching capacity of clays. KMnO4 solution on the other hand selectively destroys the unsaturated structure of the B-carotene responsible for the red colouring pigmentation of palm oil. These factors are separately responsible for the bleaching of palm oil either by adsorptive or oxidative process. These capabilities were exploited in the kinetics studies of the bleaching processes in each case.

The plots of Log A versus time were plotted and shown in graphs. Figure 1 shows the plot of log (Absorbance) against time for acidified oxidative bleaching of palm oil by $KMn0_4$ at $80^{0c}$ with slope of y= 0.0284x – 0.1561 . Figure 2 shows the plot of log (absorbance) against time for non-acidified bleaching of palm oil by $KMn0_4$ at $80^{0c}$ with slope of y = 0.0135x – 0.2761 and figure 3 shows the plot of (Absorbance) against time for bleaching of palm oil using Trona/Activate carbon blend at $80^{0c}$ with slope of y = 0.0091x – 0.0586 respectively.

A first order reaction with respect to the adsorbent and the oxidant was obtained for each case. The relevant equation used for the calculation of pertinent kinetic parameters is given as $\log (B_t/B_O) = -Kt/2.303$, where B represents the absorbance values of the bleaching agents at times t and

zero respectively. The number of adsorptive sites in the clay materials and pH of the oxidants influenced the rate of reaction. The plots of log A versus time are shown in figures 1.3. From the graphs a first order reaction is predicted. Table 3 shows the kinetics data obtained from these plots. Rate constants of $7.9 \times 10^{-2} \pm 1.4 \times 10^{-2}$ min$^{-1}$ for the acidified $KMnO_4$, $5.5 \times 10^{-2} \pm 2.0 \times 10^{-2}$ for non acidified KMnO4, $3.4 \times 10^{-2} \pm 9.0 \times 10^{-3}$ min$^{-1}$ for the trona/fullers earth blend, and $2.1 \times 10^{-2}$ for trona/activated carbon blend were obtained.

## 5. Conclusion

The acidified potassium tetraoxomanganate vii ($KMnO_4$) oxidative process had a higher bleaching efficiency than clay materials used in this study. In addition, the comparably short half-life of 10min obtained suggests that the oxidative process is better for the bleaching of palm oil. Acidified $KMnO_4$ is therefore recommended for industrial bleaching of palm oil.

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