

## Clay Characterization and Bleaching of Crude Palm Oil Using Acid-Activated Nibo Clay

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### ABSTRACT

Acid-activated Nibo clay was applied as an adsorbent in the bleaching of crude palm oil. The collected clay sample was activated with hydrochloric acid solution after it was sun-dried and ground. The raw (NC) and activated clay (ANC) samples were characterized using XRF, SEM, and FTIR analyses. The efficiency of the bleaching process was examined by varying the adsorbent dosage, temperature and the contact time. The results of XRF, SEM, and FTIR analyses on NC and ANC showed that the clays were kaolinites with significant changes after activation. The bleaching experiment showed that increase in temperature improved the efficiency of the process. The highest bleaching efficiency of 86% was observed. The pseudo-second-order model best described the adsorption process at 100 °C when compared to correlation coefficient values of the pseudo-first-order, Intra-particle diffusion and Elovich kinetic models. The Temkin isotherm model best fitted the experimental data than the Langmuir, Freundlich and Dubinin-Radushkevich models with R<sup>2</sup> values of >0.9 at all temperatures. The enthalpy and entropy values were evaluated as 54,943.90 J/mol and 154.6321 J/mol respectively. The enthalpy and entropy values indicated that the adsorption process was endothermic and showed an increase in randomness at the solid/liquid interface. The negative values of the Gibb's free energy at 363 and 373 K implied that beta carotene adsorption of crude palm oil at these temperatures was spontaneous and feasible. This experimental study showed that acid activated Nibo clay can be applied as an adsorbent for the bleaching of crude palm oil at higher temperatures.

### INTRODUCTION

Crude palm oil, a product that is obtained from the oil palm fruit is a major agricultural produce in Nigeria. Its numerous advantages include its domestic and industrial applications [1]. Its high competitiveness has increased the growth in the demand for palm oil [2]. It is a major cooking ingredient in Nigerian homes and is also used in soap-making. Its medicinal properties are seen in its remedy for cough and as an initial treatment when poisonous substances are ingested. It is also known for its ability to reduce both blood pressure and the risk of arterial thrombosis. Its industrial application is seen in its use as a raw material in the production of detergents, lubricants, margarine, cosmetics and biofuel [1]. It is very rich in carotenoids. Carotenoids in palm oil present as beta-carotene are the pigments responsible for the orange-red color of palm oil [3]. However, its richness in

carotenoids, fatty acids and impurities has limited its domestic and industrial use. Hence, the need to refine crude palm oil by adsorptive bleaching to improve its appearance, flavor, quality and stability [1,3].

Bleaching is a process which involves the adsorption of unwanted components with the use of an adsorbent in the presence of heat [1]. Activated carbon, silica and acid activated clays are common adsorbents used in the industry for bleaching purposes [2]. The adsorbent concentrates the unwanted component from the palm oil unto the surface of the solution thereby producing a more acceptable color [1,3]. Most of the adsorbents used in Nigeria are imported activated carbon and fuller earth but the enforcement by the Nigerian government to stop importation has led to the need to substitute these imported goods with locally sourced materials [1].

Clay is a highly abundant and substitutable material in Nigeria that can be used as an adsorbent [1]. The clays that can be used may be naturally active or activated clays. The adsorptive bleaching activity of naturally active clays are quite high due to their high surface area but activated clays applied for bleaching purposes show a much higher activity [4]. It has been proven that the adsorptive property of local clays can be improved by activating them with acidic or alkaline reagents [1]. Some advantages of acid-activated adsorbents include the dealumination of the structure, the removal of metal ions in the octahedral layer and opening of the platelets thereby increasing the pore diameters and surface areas [4]. Studies on the bleaching capacities of some Nigerian clays have been studied by some researchers [5,4,1].

The analyses of the adsorption of beta-carotene onto the bleaching clay can be done using adsorption kinetic modelling, equilibrium adsorption isotherm and thermodynamics studies [3]. Kinetics studies can be used to describe the solute uptake rate at the solid-solution interface, the rate of pollutant removal from the solution, and in the design of appropriate adsorption treatment plants [6]. Factors affecting bleaching processes are temperature, mass of the clay, concentration of the acid or alkaline in the clay, concentration of beta-carotene, and the clay's properties. Applying an unacceptable model to the process control can lead to the inefficient bleaching process [3]. Hence, the need to evaluate the kinetic studies on the bleaching process.

The application of Nibo clay in the bleaching of crude palm oil has not been recorded. Hence, this study was carried out to study the potentials of acid-activated Nibo clay in the bleaching of crude palm oil. Studies on the appropriate kinetic model that could analyze the bleaching process for process conditions were also carried out using the first-order, pseudo-first-order, pseudo-second-order, intra-particle diffusion model, and the Elovich equation. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models were evaluated for the isotherm studies while the thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) of the process were also estimated.

## MATERIALS AND METHODS

### Material collection and preparation

The natural clay sample was obtained from Nibo town (6.1722°N, 7.0633°E) in Awka South of Anambra state, Nigeria. The clay sample was sun-dried for 24 h, ground and sieved with a sieve of 150  $\mu\text{m}$  mesh size. The crude palm oil was sourced from a palm oil processing plant in Ifite Awka, Anambra State. Distilled water, hydrochloric acid and acetone of standard qualities were also collected for the experiment.

### Acid activation of the clay

The clay was activated using the method applied by [1]. Slurry was formed by mixing 200 g of the prepared Nibo clay sample with 250 mL of 5 M concentration of hydrochloric acid (HCl). The slurry was heated on a magnetic stirred hot plate at a temperature of 100 °C for 2 h. After heating, the slurry was cooled and the activated Nibo clay (ANC) was separated with a filter paper and a funnel. The activated clay was washed free of the acid with distilled water until a neutral point is obtained and recorded with a pH meter. The clay was then dried at a temperature of 105 °C for 24 h in the Memmert oven, ground again using laboratory mortar and pestle, and sieved with a 150  $\mu\text{m}$  mesh sieve.

### Characterization of the clay

The X-ray fluorescence (XRF) analysis was carried out to determine the concentration of the elements and percentage composition of the clay sample before and after activation [1]. The XRF analysis was determined using the X-supreme 8000 XRF spectrometer. Fourier transform infrared spectroscopy (FTIR) analysis measures the different functional groups present in the clay [2]. The FTIR of the clay sample was analyzed before and after activation with an FTIR Shimadzu S8400 spectrophotometer and were recorded in the range of 400-4000  $\text{cm}^{-1}$ . Scanning electron microscopy (SEM) analysis was done with a scanning electron microscope of PW 100-002 model at a magnification of 225x. SEM analysis was carried out to evaluate the surface morphology of the clay sample before and after activation [2].

### Bleaching process

100 mL of the degummed crude palm oil was poured into a 500 mL pyrex beaker and magnetic hot plate set at the required temperature. As the set temperature was reached, a measured quantity of the activated clay (1 g) was introduced into the beaker. Little quantities of the oil were withdrawn after contact times of 10, 20, 30, 40, 45, and 50 min and the samples were diluted in acetone to a concentration of 10% (v/v). The sample was filtered and the absorbance ( $A_t$ ) measured using a UV spectrophotometer (model no - 752, P/N: C001) at a wavelength of 450 nm [7,8]. The absorbance reading was applied in evaluating the efficiency of the bleaching process using equation (1).

$$\text{Bleaching performance (\%)} = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

Where  $A_0$  and  $A_t$  are the absorbances of crude palm oil and bleached palm oil at time  $t$  respectively. The effect of contact time on the bleaching efficiency of ANC was tested with four kinetic models as shown in **Table 1** and several isothermal models (**Table 2**) to evaluate the mechanism controlling the adsorption process.

**Table 1.** Adsorption kinetic models fitted into the bleaching process using ANC.

Kinetic model	Kinetic equation	Reference
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - K_1 t$ (2)	[9]
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + t \left(\frac{1}{q_e}\right)$ (3)	[2]
Intra-particle	$q_t = K_d t^{0.5} + \varepsilon$ (4)	[9]
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$ (5)	[10]

To investigate the equilibrium adsorption studies on the bleaching efficiency of the activated clay sample, the bleaching process was carried out at different masses of the activated clay [8]. 100 mL of the crude palm oil was put in a 500 mL beaker, placed on a hot plate and heated to the desired temperature. The weighed activated clay was added and the mixture was continuously heated and stirred. At the end of the bleaching process, the mixture was allowed to cool, and clay mixture was filtered before the absorbance reading was taken using a UV spectrophotometer. The experiment was performed at different masses of the adsorbent (activated clay) which was varied at 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0 g by weight. This experiment was carried out at the temperature of 100 °C and contact times of 10, 20, 30, 40, 45, and 50 min.

**Table 2.** Equilibrium isotherm models fitted into the bleaching process using ANC.

Isotherm model	Isotherm equation	Reference
Langmuir	$\frac{x_e}{q_e} = \frac{1}{K_1 q_m} + \frac{x_e}{q_m}$ (6)	[9]
Freundlich	$\log q_e = \log K + \frac{1}{n} \log X_e$ (7)	[10]
Temkin	$q_e = B_1 \ln K_T + B_1 \ln X_e$ (8)	[9]
Dubinin-Radushkevich (D-R)	$\ln q_e = \ln Q_m - \beta \varepsilon^2$ (9)	[11]
	$\varepsilon = RT \ln(1 + \frac{1}{C_e})$ (10)	
	$E = \frac{1}{(\sqrt{2\beta})}$ (11)	

### Adsorption thermodynamics

Parameters evaluated from thermodynamic studies indicate whether the process is spontaneous, non-spontaneous, exothermic or endothermic thereby aiding in the design of an adsorption process [12]. The thermodynamic parameters which were the standard Gibb's free energy change ( $\Delta G$ ), the standard enthalpy change ( $\Delta H$ ) and the standard entropy change ( $\Delta S$ ) were calculated using Equations (12), (13), (14) and (15).

$$\Delta G^\circ = RT \ln(k_d) \quad (12)$$

Where,

$\Delta G^\circ$  (J/mol) is the Gibb's free energy change, R is the universal gas constant (8.314 Jmol<sup>-1</sup>K<sup>-1</sup>), T is the absolute temperature (K) and  $k_d$  is the thermodynamic equilibrium constant.

$$k_d = \frac{q_e}{X_e} \quad (13)$$

$$\ln k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (14)$$

$$\Delta G = \Delta H - T\Delta S \quad (15)$$

The enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) values both in (J/mol) are estimated from equation (14) whereas the values of  $\Delta G^\circ$  is calculated from Equation (15) [4]. Using Equation (14),  $\ln k_d$  was plotted against  $1/T$  where the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and intercept of the linear plot.

## RESULTS AND DISCUSSION

### Clay characterization

#### X-ray Fluorescence (XRF) analysis

The chemical compositions of raw and activated Nibo clays were determined by XRF spectrometry. The result obtained as seen in **Table 3** showed that the major oxides present in the clay samples were SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. The clay was seen to have a high content of silica oxide (up to 56%), indicating that it can be used for the production of floor tiles [13]. However, the dominant oxides were silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) as also reported by [14]. [15] stated that the presence of these dominant oxides indicated that both clays were kaolins (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>). The concentrations of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and MnO were also observed to increase slightly after activation. The content of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was higher in the raw clay than activated clay. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio in the activated clay was lesser than 2 indicating reduction of SiO<sub>2</sub> in the form of quartz and the absence of montmorillonite in the clay [14]. The XRF data also revealed the presence of several elements which included oxygen, aluminum, iron and silicon (**Table 4**).

**Table 3.** XRF result of oxides from raw and activated Nibo clay.

Oxide	Concentration in % (before activation)	Concentration in % (after activation)
SiO <sub>2</sub>	76.470	50.315
V <sub>2</sub> O <sub>5</sub>	0.077	0.158
Cr <sub>2</sub> O <sub>3</sub>	0.079	0.025
MnO	0.031	0.112
Fe <sub>2</sub> O <sub>3</sub>	1.592	18.583
CO <sub>3</sub> O <sub>4</sub>	0.013	0.086
NiO	0.003	0.000
CuO	0.047	0.036
Nb <sub>2</sub> O <sub>3</sub>	0.019	0.014
MoO <sub>3</sub>	0.005	0.005
WO <sub>3</sub>	0.004	0.000
P <sub>2</sub> O <sub>5</sub>	0.000	0.062
SO <sub>3</sub>	0.071	0.108
CaO	0.043	0.414
MgO	0.000	0.000
K <sub>2</sub> O	0.032	0.356
BaO	0.034	0.000
Al <sub>2</sub> O <sub>3</sub>	17.207	25.999
Ta <sub>2</sub> O <sub>5</sub>	0.038	0.012
TiO <sub>2</sub>	2.741	2.694
ZnO	0.001	0.006
Ag <sub>2</sub> O	0.015	0.013
Cl	0.750	0.645
ZrO <sub>2</sub>	0.429	0.308
SnO <sub>2</sub>	0.000	0.000
PbO	0.007	0.023
Rb <sub>2</sub> O	0.002	0.012
SrO	0.008	0.016

**Table 4.** XRF result of element from raw and activated Nibo clays.

Element	Concentration in % (before activation)	Concentration in % (after activation)
O	50.719	46.203
Mg	0.000	0.000
Al	9.107	13.760
Si	35.745	23.519
P	0.000	0.027
S	0.028	0.043
Cl	0.750	0.645
K	0.261	0.296
Ca	0.030	0.296
Ti	1.643	1.615
V	0.043	0.089
Cr	0.054	0.017
Mn	0.024	0.087
Fe	1.114	12.997
CO	0.010	0.063
Ni	0.003	0.000
Cu	0.038	0.029
Zn	0.001	0.005
Rb	0.001	0.011
Sr	0.007	0.013
Zr	0.317	0.228
Nb	0.015	0.011
MO	0.004	0.003
Ag	0.014	0.012
Sn	0.000	0.000
Ba	0.030	0.000
Ta	0.031	0.010
W	0.003	0.000
Pb	0.006	0.021

### Scanning electron microscopy (SEM)

Figs. 1 and 2 showed the result of the SEM analysis of the raw and acid-activated clays respectively. This analysis observes the morphological structure, texture and the surface topography of the adsorbent before and after activation [13]. From the results, it was observed that the structure of the raw clay (NC) was coarse, loosely packs with well-formed flakes and irregular hexagonal edges, an indication that they were kaolinites [13]. Their particles were coarse and not well crystalized as a result of the high silica and aluminium content of the clays observed from their chemical composition [16]. The pores and surface areas of NC were observed to become more developed after activation [17].

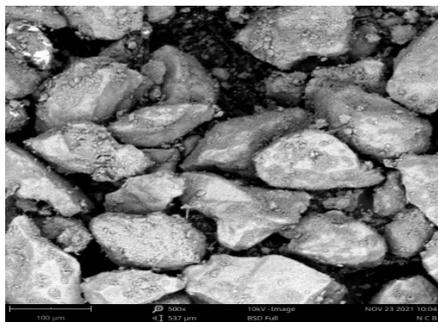


Fig. 1. SEM analysis of Nibo clay (NC) before activation (100  $\mu\text{m}$ ).

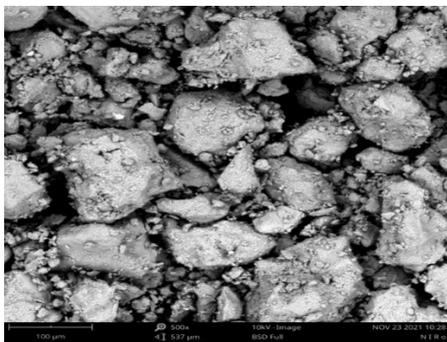


Fig. 2. SEM analysis of Nibo clay (ANC) after activation (100  $\mu\text{m}$ ).

### Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra were obtained for NC and ANC was carried out at the wavenumber range of 650 – 4000  $\text{cm}^{-1}$ . The interpretation of the FTIR results of NC and ANC were carried out according to the reports by [18-21]. The FTIR results for NC and ANC are shown in Figs. 3 and 4 respectively. The results obtained indicated that there were disappearances and appearances of some functional groups due to clay activation as observed by other researchers [19].

Some of the functional groups that disappeared from the raw clay after activation were Alkenyl C=C stretch (1625.1), N-H bend (1569.2), methyl C-H bend (1453.7 and 1375.4) and O-H in-plane bend (1334.4) [18,19,21]. The dominant presence of kaolinite mineral was detected by the relative intensity of O-H stretching bands in the FTIR spectrum [22].

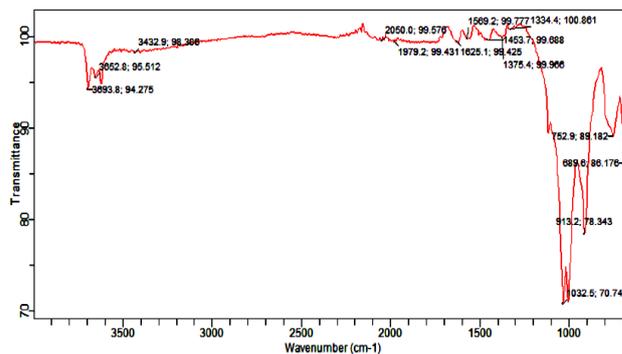


Fig. 3. FTIR of raw Nibo clay (NC).

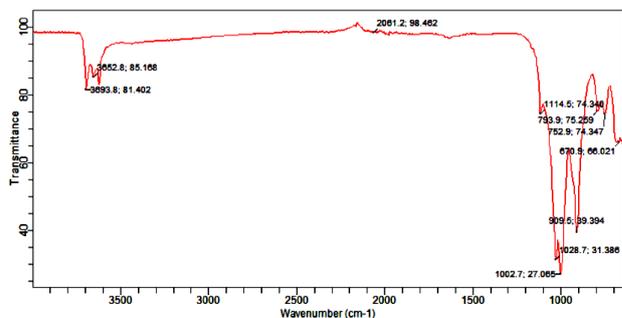


Fig. 4. FTIR of activated Nibo clay (ANC)

### Batch studies of the bleaching process

#### Effect of temperature and contact time on the bleaching efficiency

At constant mass of 1 g, and initial absorbance reading of 2.50, the temperature of the bleaching process was varied at 50, 70, 90 and 100  $^{\circ}\text{C}$  at different time intervals between 10 to 50 mins. Optimum bleaching performance of 82% was observed for 100  $^{\circ}\text{C}$  at 50 mins. Observations revealed that the absorbance and bleaching efficiency reduced and increased respectively with increase in the temperature. The bleaching efficiency of ANC was also observed to increase rapidly at first but reduced after 40 mins. This was because the vacant sites decreased as the contact time of the bleaching process increased [1,8]. From the results obtained, it can be said that higher temperatures improved the bleaching efficiency as the contact time increased [4,1]. It was also observed that the bleaching efficiency also increased with increase in time [23]. Fig. 5 showed the plots of the bleaching efficiencies with increase in temperature and time.

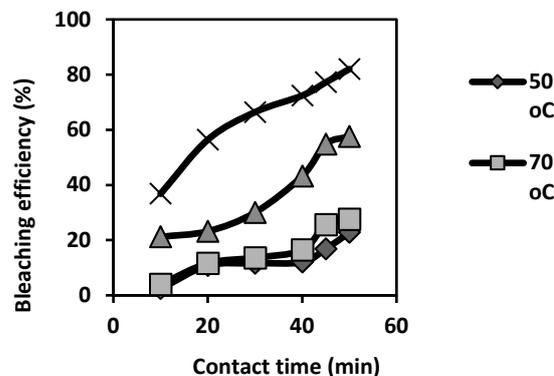


Fig. 5. Effect of temperature and contact time on the bleaching efficiency of ANC on crude palm oil.

### Effect of dosage and contact time on the bleaching efficiency

The plot of the bleaching efficiencies as temperature and contact time is varied in seen in Fig. 6. It was observed that the absorbance and bleaching efficiency generally increased with increase in ANC dosage [24-26,4]. This was due to the increase in the surface area of the adsorbent leading to the increase in the pore spaces of the active adsorption site [25]. However, at 4 g the bleaching efficiency remained constant and dropped as the contact time increased and could have been due to the complete adsorption of the color pigments (beta carotene) onto the available active sites of the adsorbent [26]. A maximum dosage of 4.0 g was observed for acid-activated Nibo with percentage color reduction of 86.0% at 40 min. Beyond this, further increase in clay dosage did not increase the bleaching efficiency [4]. This indicated that the adsorption had reached equilibrium at that point [25].

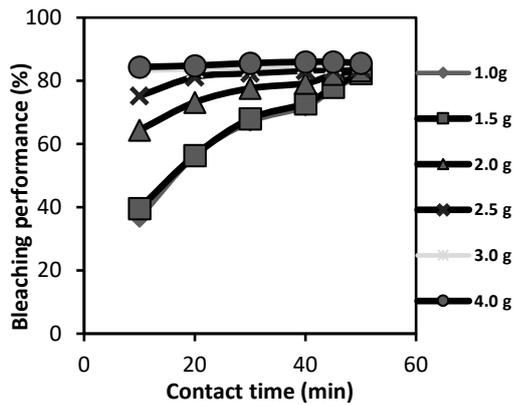


Fig. 6. Effect of adsorbent dosage and contact time on the bleaching efficiency of ANC on crude palm oil

### Kinetic modelling of the bleaching process

The kinetic modeling of crude palm oil bleaching using ANC was analyzed using four models namely pseudo-first order, pseudo-second order, intra-particle and Elovich models. The comparison of the data analyses was based on the regression coefficient values ( $R^2$ ) obtained from the linear plots of the model equations as shown in Figs. 7-10. The constants evaluated from the model plots are tabulated in Table 5. The results indicated that the experimental data was best described by the pseudo second-order kinetic model following its best fitness with the correlation coefficient ( $R^2$ ) value of 0.9976 at 100 °C [4] and [27] also reported that the pseudo second-order kinetic model best described the experimental bleaching process of palm oil. The Elovich model also provided a good fit at 100 °C with a high  $R^2$  value of 0.9971 [25] reported a good fit of adsorption process of lead (II) ion in wastewater using Elovich model.

The intra-particle model was not the sole controlling step for describing the kinetic process as the linear plot of  $q_t$  versus  $t^{0.5}$  did not pass through the origin [1]. The bleaching temperatures of 50, 70 and 90 °C did not provide good fits to the experimental data as observed from their low correlation coefficient ( $R^2$ ) values and hence only the bleaching temperature of 100 °C represented the system.

This observation was made for all the kinetic models including the pseudo-first-order model. With this result, it can be concluded that process temperature did not only affect the process speed but also affected the maximum adsorption capacity [25]. The amount of  $\beta$ -carotene adsorbed (mg/g) at equilibrium ( $q_e$ ) increased as the bleaching temperature increased [4].

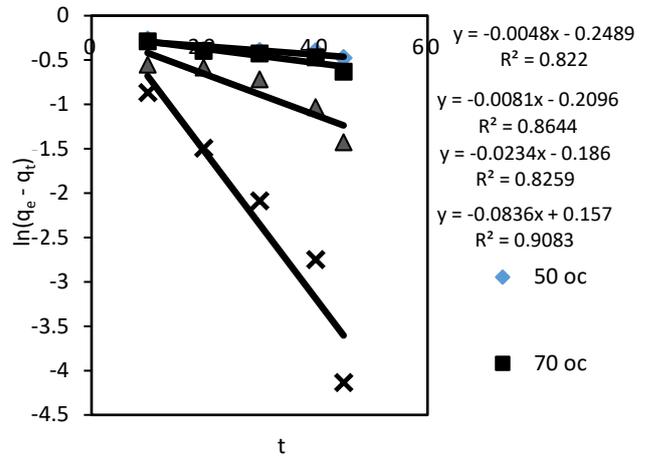


Fig. 7. Plot of Pseudo first-order kinetic model.

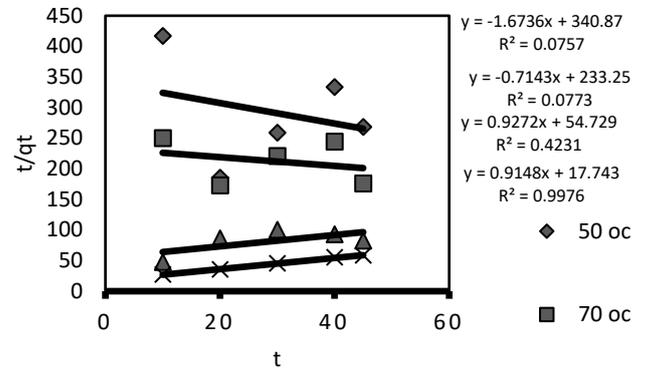


Fig. 8. Plot of Pseudo second-order kinetic model.

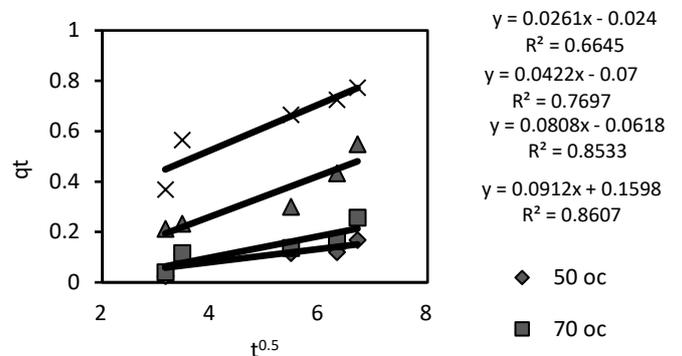


Fig. 9. Plot of Intra-particle diffusion kinetic model.

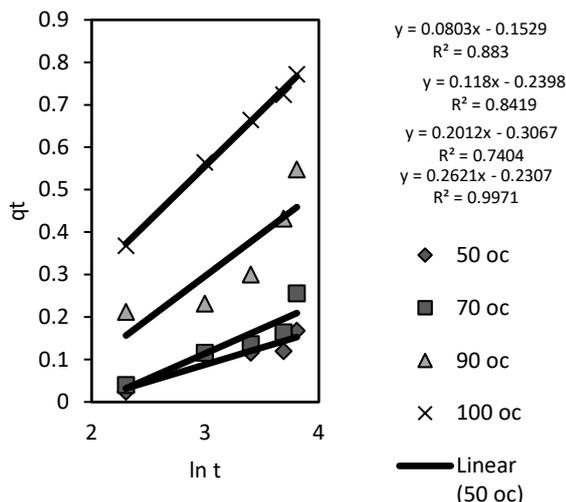


Fig. 10. Plot of Elovich kinetic model.

Table 5. Adsorption kinetic parameters for the bleaching of palm oil using ANC.

Kinetic model	Kinetic constants	Temperature (°C)			
		50	70	90	100
Pseudo first-order	$K_1$ ( $\text{min}^{-1}$ )	0.0048	0.0081	0.0234	0.0836
	$q_e$ (mg/g)	0.7797	0.8109	0.8303	0.8547
	$R^2$	0.8220	0.8644	0.8259	0.9083
Pseudo second-order	$K_2$ ( $\text{g/mg} \cdot 7.1047 \times 10^4$ )	-7.5715 $\times 10^4$	-7.5715 $\times 10^4$	3.2195 $\times 10^3$	3.4365 $\times 10^2$
	$q_e$ (mg/g)	0.0029	0.0043	0.0183	0.0564
	$R^2$	0.0757	0.0773	0.4231	0.9976
Intra-particle diffusion	$K_d$	0.0261	0.0422	0.0808	0.0912
	$\epsilon$	-0.024	-0.070	-0.0618	0.1598
	$R^2$	0.6645	0.7697	0.8533	0.8607
Elovich	$\alpha$	0.0120	0.0155	0.0438	0.1087
	$\beta$	12.4533	8.4746	4.9702	3.8153
	$R^2$	0.8830	0.8419	0.7404	0.9971

### Equilibrium Isotherm modelling of ANC on crude palm oil bleaching

The study of equilibrium adsorption isotherm is very important in the design of adsorption systems [18]. The fitness of the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models at varying temperatures were investigated and the evaluated constants and coefficient of correlation ( $R^2$ ) were listed in Table 6. The model with the best  $R^2$  value was taken as the best fitting model for the experimental data. The correlation coefficients  $R^2$  of the Langmuir and Freundlich models were low (<0.9) at 50 and 70 °C for the adsorption of free fatty acids. For the Langmuir model, the lowest value of the maximum adsorption capacity ( $q_m$ ), indicating the complete coverage of the adsorbent surface by the adsorbate, was obtained at 50 °C. However, Langmuir model did not give a good accuracy at this temperature due to the low  $R^2$  value. The Langmuir constant,  $K_L$ , presented a positive correlation with temperature as increase in temperature increased the value of  $K_L$ , hence increasing the affinity between the adsorbent and adsorbate [12]. For the Freundlich model, the values of the constant  $n$  being greater than 1, describe good affinity between the pigments and the activated clay surface. In this case, the values of  $n$  were less than 1 at all temperatures indicating that the affinity between the acid-activated clay and pigment was not good enough [16].

The  $R^2$  values were also low in Dubinin-Radushkevich model at 50, 70 and 100 °C. This suggested that this model is not suitable for describing the adsorption of free fatty acids of vegetable oils analyzed in this study. The Dubinin-Radushkevich isotherm relates to the degree of the adsorption of the adsorbate on the adsorbent surface. The model determines the apparent energy of heterogeneous surface systems. 'E' represents the apparent energy of adsorption. The value of E (KJ/mol) was greater than 8 kJ/mol indicating chemisorption [28].

The Temkin isotherm model which gave the best fitting with  $R^2$  values of >0.9 at all temperatures for the adsorption was observed as the most suitable model for the adsorption of free fatty acids. It has also been reported that Temkin model is the most accepted isotherm model [16,4,27]. The lower values obtained for the constant  $b$  at 50, 70 and 90 °C indicated that the interaction between pigments and clay was strongest at 100 °C [16].

Table 6. Equilibrium isotherm parameters for the bleaching of crude palm oil using ANC.

Adsorption isotherm model	Kinetic constants	Temperature (°C)			
		50	70	90	100
Langmuir	$K_L$ (l/mg)	0.8074	0.7291	0.3576	0.1514
	$q_m$ (mg/g)	0.0072	0.0181	0.3551	2.0016
	$R^2$	0.6807	0.7037	0.9496	0.9526
Freundlich	$K$ (l/g)	$6.84 \times 10^{-10}$	$7.16 \times 10^{-7}$	0.0263	0.2395
	$n$	-0.6541	-0.7413	-1.2480	-1.9681
	$R^2$	0.8459	0.8831	0.9675	0.9130
Temkin	$K_T$ (mg/g)	0.9921	0.8683	4.7702	8.3055
	$b$ (KJ/mol)	-3.0942	-3.4428	5.1370	8.6745
	$R^2$	0.9981	0.9982	0.9951	0.9647
Dubinin-Radushkevich (D-R)	$Q_m$ (mg/g)	0.0002	0.0018	0.1052	0.3468
	$\beta$	$-2.0 \times 10^{-6}$	$-9.0 \times 10^{-7}$	$-1.0 \times 10^{-7}$	$-3.0 \times 10^{-8}$
	E (KJ/mol)	500	745.36	2236.07	4082.48
	$R^2$	0.809	0.8518	0.9392	0.8126

### Adsorption Thermodynamics

The thermodynamics study of an adsorption process gives an indication of the spontaneity of the process. Spontaneous reaction is said to have occurred if a negative value of  $\Delta G^\circ$  is obtained at a given temperature [4,6]. The thermodynamic plot and values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  obtained from the adsorption of beta carotene from crude palm oil onto ANC are shown in Fig. 11 and Table 7, respectively. The negative values of  $\Delta G^\circ$  obtained at 363 and 373 K implied that beta carotene adsorption of crude palm oil onto ANC at 363 and 373 K was spontaneous and feasible [2]. The bleaching process was observed to be non-spontaneous at 323 and 343 K due to the positive values of  $\Delta G^\circ$  obtained. This indicated that the bleaching of crude palm oil using ANC was more favorable at temperatures higher than 323 and 343 K [2,4].

The value of  $\Delta H^\circ$  was evaluated as 54,943.90 J/mol. The positive value of  $\Delta H^\circ$  indicated that the chemical adsorption process of beta carotene onto ANC was endothermic between the temperature range of 323 - 373 K. This showed that an improvement in the adsorption process would be seen as the temperature is increased [2]. A positive value of 154.6321 J/mol was obtained as  $\Delta S^\circ$  which showed an increase in randomness at the solid/liquid interface during the adsorption process [4]. The positive values of enthalpy and entropy indicated that all the regions of ANC were favorable [2].

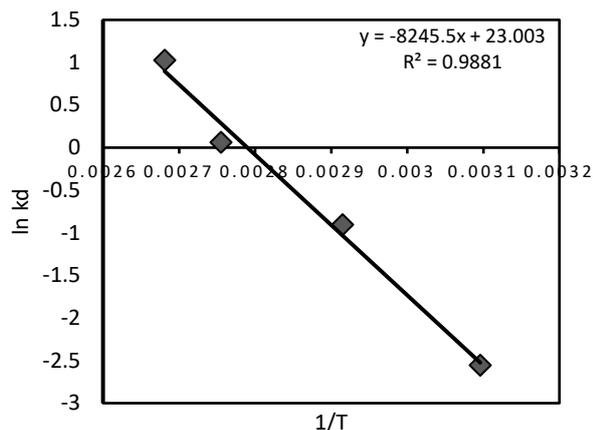


Fig. 11. Thermodynamics plot of crude palm oil bleaching with ANC.

Table 7. Parameters of thermodynamic study of palm oil bleaching with ANC.

Temperature (K)	Thermodynamic properties		
	$\Delta G^0$ (J/mol)	$\Delta H$ (J/mol)	$\Delta S$ (J/mol)
323	4,997.7317	54,943.90	154.6321
343	1,905.0897		
363	-1,187.5523		
373	-3,000.00		

## CONCLUSION

The adsorption of beta carotene from crude palm oil was successfully carried out through bleaching process using acid activated Nibo clay. The characterization of Nibo clay indicated that the clay was kaolinite. Increase in adsorbent dosage, temperature and contact time increased the performance of the bleaching process. The highest bleaching efficiency of 86% was obtained from the process. The pseudo second-order kinetic model best described the bleaching process at 100 °C. The Temkin isotherm model best fitted the equilibrium data at all temperatures when compared to other isotherm models. The thermodynamic study revealed that the bleaching of crude palm oil with ANC was endothermic, spontaneous and suggested chemisorption. The results of this experiment indicated that ANC can be applied as a potential commercial adsorbent for the bleaching of crude palm oil, thereby improving the economy of the country.

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