

EQUILIBRIUM, KINETICS AND THERMODYNAMICS OF THE BLEACHING OF PALM OIL USING NANDO CLAY

ABSTRACT

The effectiveness of Nando clay in the bleaching of palm oil was studied in this work. The clay was prepared by activating it with hydrochloric acid. The bleaching was carried out at different temperatures, adsorbent dosage and particle sizes. The result suggests that increase in temperature and adsorbent dosage increases the bleaching efficiency while increase in particle size decreases the bleaching efficiency. Both the pseudo-first-order and the pseudo-second-order kinetic models describe efficiently the experimental data of the bleaching process. Intra-particle diffusion though involved in the adsorptive bleaching mechanism, is not the sole rate-limiting step in the bleaching of palm oil with activated Nando clay. The equilibrium data were described better by Langmuir and Freundlich models. The thermodynamic study revealed that the adsorptive bleaching process is endothermic, spontaneous with an increase in entropy.

Keywords: Nando clay, palm oil, adsorption, bleaching, isotherm, kinetics

1. INTRODUCTION

Palm oil is one of the numerous products that can be obtained from the oil palm fruit. The oil palm fruit is made up of an outer skin (the exocarp), a pulp (mesocarp) containing the palm oil in a fibrous matrix; a central nut consisting of a shell (endocarp); and the kernel, which itself contains an oil, quite different to palm oil, resembling coconut oil [1]. Crude palm oil is one of the major agricultural products for which Nigeria is well known for. Palm oil is well

30 known for its domestic and industrial applications. In homes, palm oil is a major cooking
31 ingredient used in preparing different kinds of delicacies. It is used also in making soap. In
32 most households in Nigeria, it serves as a remedy for cough and as an initial treatment when
33 poisonous substances are ingested. Industrially, it serves as one of the raw materials in
34 preparing some products such as margarine, detergents, lubricants, cosmetics and production
35 of biofuel [2,3]. Medically, palm oil is important in the reduction of both blood pressure and
36 the risk of arterial thrombosis [4,5].

37 Palm oil is rich in carotenoids, (pigment found in plants and animals) from which it derives
38 its deep red color. It also contains glycerides of the saturated fatty acid hence it is viscous
39 semi-solid, even at tropical ambient and a solid fat in temperate climates. The presence of
40 carotene, fatty acids, impurities etc has been found to limit its usage both domestically and
41 industrially. Hence, one of the steps in the refining of oil involves the removal of these
42 substances in the process of adsorptive bleaching to improve the stability, appearance and the
43 sensory quality of the palm oil.

44 Bleaching is an adsorption process which involves the use of adsorbents in removing
45 undesirable oil components [6]. It is based on the ability of an adsorbent to preferentially
46 concentrate specific substances from solutions unto their surfaces. In Nigeria, most of these
47 adsorbents are usually imported as fuller earth and activated carbon but the recent drive of the
48 Federal government to reduce importation and increase the use of locally sourced materials
49 have led to increased research on substitutes for these adsorbents [1].

50 Clay is abundant in large deposit in most parts of Nigeria. Clay is readily available in large
51 quantity and its potentials have not been clearly defined and put into proper use. It has been
52 proved that the adsorbing capacity of clay can be increased by activating the clay. Clays are
53 non- renewable resources. Different clays in Nigeria, have been studied in recent times for
54 their bleaching abilities [7,8,9]. So far, there has been no record of Nando clay being used in

bleaching studies though it has a large deposit in Nigeria. Its potentials have not been fully utilized. Hence, this present study is aimed at studying the potentials of Nando clay in bleaching of palm oil.

58

59 **2. MATERIALS AND METHODS**

The natural clay sample was obtained from Nando village (6.3°N, 6.9°E) in Anambra state, Nigeria. The palm oil was sourced from oil processing plant in Awka, Anambra State. The distilled water, phosphoric acid, sodium hydroxide used were all of analytical grade.

63 **2.1 Acid activation of the clay**

The clay was activated according to the method used by [10]. The clay material was first prepared for activation by drying it under the sun at an ambient temperature of 35°C to make it amenable to grinding. The clay sample was then reduced to small size by grinding with a laboratory mortar and pestle and sieved to a particle size of 300µm. 50g of the clay sample was mixed with 250ml of the prepared hydrochloric acid. The resulting suspension was heated on a magnetically stirred hot plate at a temperature of 98°C for 2.0 hours. After cooling, the clay and acid were separated by pouring the resulting slurry in a Buchner funnel with a filter paper to aid the separation. The clay residue was washed free of the acid several times with distilled water until a neutral point is obtained with pH meter. The clay was then dried at a temperature of 110°C for 3 hours, then ground again using laboratory mortar and pestle, sieved at different sizes.

75 **2.2 Bleaching process**

The crude palm oil was first degummed using phosphoric acid and distilled water and then neutralized using sodium hydroxide according to the method of [1].

The absorbance of the unbleached oil is measured (A_0). 100ml of the degummed and neutralized oil was then poured into a 500ml pyrex beaker which was then placed on a

magnetic hot plate set at an appropriate temperature. After about 20 minutes when the temperature has stabilized, measured quantity of the activated clay is introduced into the beaker. At regular time intervals, little quantity of the oil is withdrawn and the absorbance measured (A_t). This continues till when there is no significant change in the absorbance value with respect to time. The absorbance is measured using UV spectrophotometer at 445nm using the method of [10].

The efficiency of the bleaching process is measured in terms of the absorbance and expressed as a percentage using equation (1).

$$\text{Adsorptive bleaching efficiency} = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

Where A_0 is the absorbance of unbleached oil, A_t is the absorbance at time t .

The bleaching process was carried out at different adsorbent dosages (0.5g, 1.0g, 1.5g and 2.0g), different temperatures (70, 80, 90, 100, 110°C) and different particle sizes (600 μ m, 300 μ m, 150 μ m, and 75 μ m).

2.3 Physical properties

Some of the physical properties of the clay were determined by the method of [10].

2.4 Kinetics and isotherm studies

Standard linear form of some kinetic models and isotherm models were used to describe the adsorptive bleaching process [14]

2.5 Thermodynamics studies

These thermodynamic properties were determined by applying the relations

$$\Delta G^\circ = -RT \ln K_L \quad (2)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

Where ΔG° is the standard free energy change (J/mol), R is the universal gas constant (8.314 J/mol K), K_L is the Freundlich constant and T is the absolute temperature (K).

3. RESULTS AND DISCUSSION

3.1 Physical properties

Table 1 shows some of the physical properties of Nando clay both before and after activation.

The surface area increased from 194 to 541 m²/g after activation. One of the major aims of activation is to increase the surface area of the adsorbent.

The pH of the clay became acidic after activation. This is probably because the acid that was used in the activation penetrated into the pores of the molecules of the clay. This was reduced to almost neutral when the activated clay was washed several times with distilled water.

The moisture content and the ash content decreased after activation. The moisture content measures the quantity of moisture in the clay while ash content measures the organic content in the clay

Table 1. Physical Properties of the clay

Parameter	Unactivated NC	ANC
Surface Area (m ² /g)	194	541
pH	8.3	4.4
Moisture content (%)	13.2	11.3
Ash content (%)	25.00	14.81

3.2 X-ray Fluorescence (XRF)

The mineral oxides present in the clay were determined using the XRF analysis. The result indicates that Nando clay has a high silicon oxide content as seen in Table 2. Other oxides with high concentrations were aluminum oxide and iron II oxide. [11] got similar results with

122 Nteje clay. There were also traces of other oxides such as oxides of calcium, zinc, nickel, and
 123 copper among others.

124 Table 2. Result of XRF analysis of Nando clay

Chemical composition	Natural Nando clay (%)	Activated Nando clay (%)
SiO ₂	58.89	67.41
Fe ₂ O ₃	10.11	5.90
Al ₂ O ₃	23.7	17.89
CaO	2.08	0.91
MgO	1.03	0.43
K ₂ O	0.12	0.04
TiO ₂	5.88	3.02
CaO	0.18	0.09
MnO	0.061	0.041
V ₂ O ₅	0.24	0.11
Cr ₂ O ₃	0.089	0.064
ZnO	0.010	0.002
NiO	0.026	0.004
CuO	0.039	0.006
LOI	4.14	2.34

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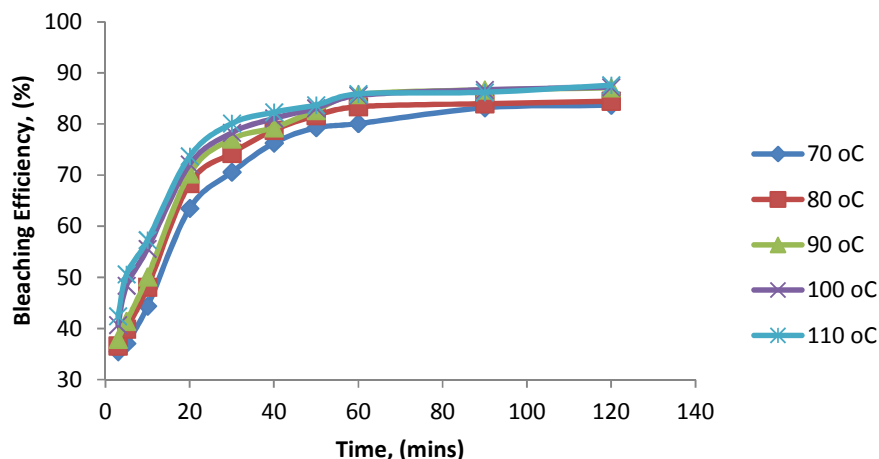
126 3.3 Batch studies

127 The batch studies were carried out to determine the effects of contact time, particle size,
 128 adsorbent dosage and temperature on the bleaching efficiency.

129 3.3.1 Effects of contact time on bleaching efficiency

130 The bleaching efficiency of the adsorbent was observed to have increased very fast in the first
 131 20 minutes and then gradually slowed down as seen in Figure 1. This can be attributed to the
 132 vast surface sites at the initial stage of the bleaching process. After the initial rapid adsorption
 133 of the carotene pigments, the bleaching efficiency increased at a much slower rate until it

became steady. This is probably because the number of vacant sites was gradually reduced as the bleaching process progresses. This trend is in agreement with the reports of some researchers [6, 12, 13].



137

138 Figure 1: Effect of time on the bleaching efficiency of Palm oil

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140 3.3.2 Effect of Temperature and dosage on bleaching efficiency

141 Increase in temperature was found to increase the bleaching efficiency though the rate of the
 142 increase is small with respect to the temperature increase (Figure 2). This is due to the
 143 increased kinetic energy of the molecules which leads to increase in the adsorption of the
 144 pigments. Also increase in temperature promotes better access to the adsorption sites in the
 145 adsorbent [12]. It has been reported that increase in temperature results in a decrease in the
 146 oil viscosity. This results in better dispersion of the adsorbent particles, improved adsorbent-
 147 oil interactions and also less resistance to flow [1].

148 The bleaching efficiency increased as the temperature increased from 70°C to 100°C.
 149 Between 100°C and 110°C, the increase in the bleaching efficiency was not significant and
 150 beyond 110°C, the bleaching efficiency starts to decrease. [14] reported that this trend is as a
 151 result of the undesirable structural changes of the oil molecule through oxidation degradation

and isomerization. [1] reported similar trend. Further increase in temperature was observed to darken the color of the bleached oil.

The adsorbent dosage also varied from 0.5g to 4.0g. The increase in bleaching efficiency as the adsorbent dosage increased is as a result of an increase in the number of active sites available for adsorption [6]. It was observed that using adsorbent dosage above 1.5g result in an only slight increase in the bleaching efficiency. Therefore, such increase in adsorbent dosage is not economical. [14] explained that this may be due to the complete adsorption of the color pigments to the available active sites on the adsorbent.

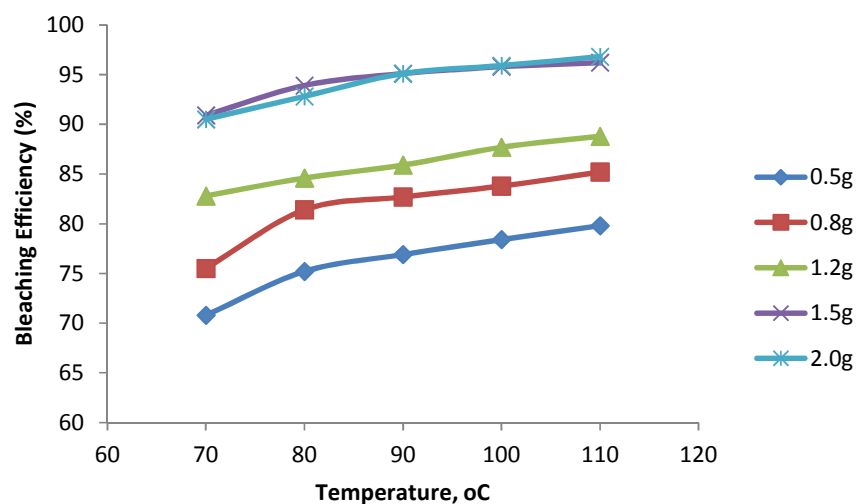


Figure 2: Effect of Temperature and dosage on the bleaching efficiency of Palm oil

3.3.3 Effect of particle size on bleaching efficiency

The bleaching efficiency was observed to have an inverse relationship with the particle size hence, as the particle size increased, the bleaching efficiency decreased. This could be attributed to the larger surface area available for contact on the surface of the adsorbent which then results in an increase in the number of active sites hence, the rate of adsorption of the color pigments increases resulting to increase in the bleaching efficiency [14]. As the particle size decreased, there was a subsequent increase in the surface area, pore volume and

pore size of the particles. This is because the reduced particle size creates more adsorption sites/cation exchange sites that are exposed to the adsorbate.

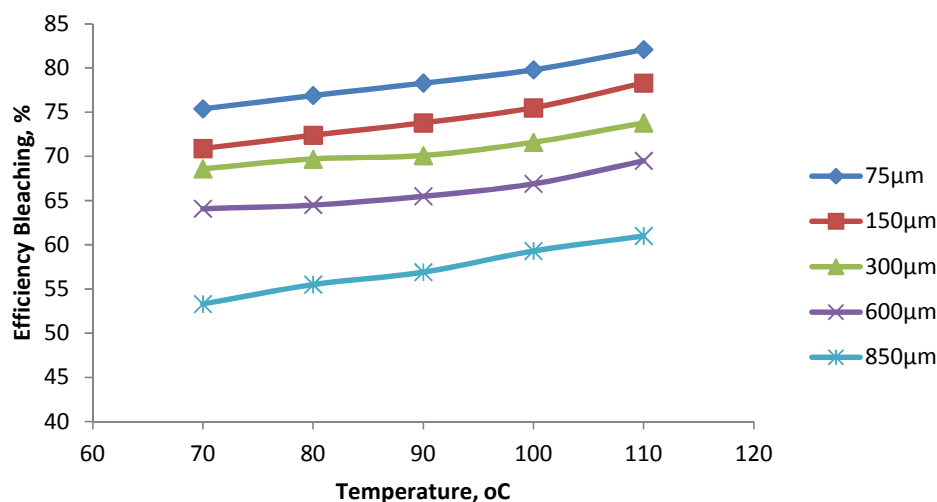


Figure3: Effect of particle size on the bleaching efficiency of Palm oil

3.4 Properties of the palm oil

Both the unbleached and the bleached palm oil were analyzed to determine its properties (Table 3). The moisture content, free fatty acid, and viscosity decreased after the bleaching on account of the heat that was used in the bleaching process. A low value of the moisture content prevents the free fatty acid from increasing through autocatalytic reactions [2]. The low value of the moisture content is responsible for the low free fatty acid. The low value of the free fatty acid also suggested that the crude palm oil used was fresh while the saponification value of 185 – 200mgKOH/kg indicated that the palm oil can actually be used in manufacturing soap. The iodine value (less than 125) showed that the palm oil is a non-drying oil [6].

188 Table 3: Properties of the palm oil

Property	Unbleached palm oil	Bleached palm oil
Moisture content (%)	3.03	1.74
Free fatty acid (%)	4.96	2.50
Iodine value (g/100g)	77	55.2
Saponification value (mg/g)	185	200
Peroxide value (mol/kg)	7.30	1.09
Refractive Index	1.50	1.07
Density (g/cm ³)	0.91	0.68
Colour	Orange Red	Orange Yellow
Viscosity	11.80	5.80

189

190

191 3.5 Kinetic Models

192 The kinetic of sorption reveals the solute uptake rate of the reaction. It is one of the important
193 characteristics in defining the efficiency of adsorption [15].

194 3.5.1 Pseudo-First Order Kinetic Model

195 The Pseudo-first order rate expression is given as:

$$196 \ln(q_e - q_t) = \ln q_e - K_1 t \quad (2)$$

197 Where q_e and q_t are the amounts of carotene adsorbed at equilibrium time and at any time t ,
198 respectively (mg/g), K_1 is the Pseudo-first order adsorption rate constant (min^{-1}), and t is the
199 contact time (min). Plots of $\log(q_e - q_t)$ against t in figure 4 were used to express the pseudo-
200 first-order at different temperatures from where q_e and K_1 were evaluated from the slope and
201 intercept respectively. The correlation coefficient values (R^2) were all greater than 0.99

indicating good correlation. The calculated q_e was found to be close to the experimental q_e . It has been reported that if the values of q_e calculated were not very close to the experimental value of q_e , the adsorption is assumed not to have followed the kinetic model even if it has a high correlation coefficient R^2 value [16].

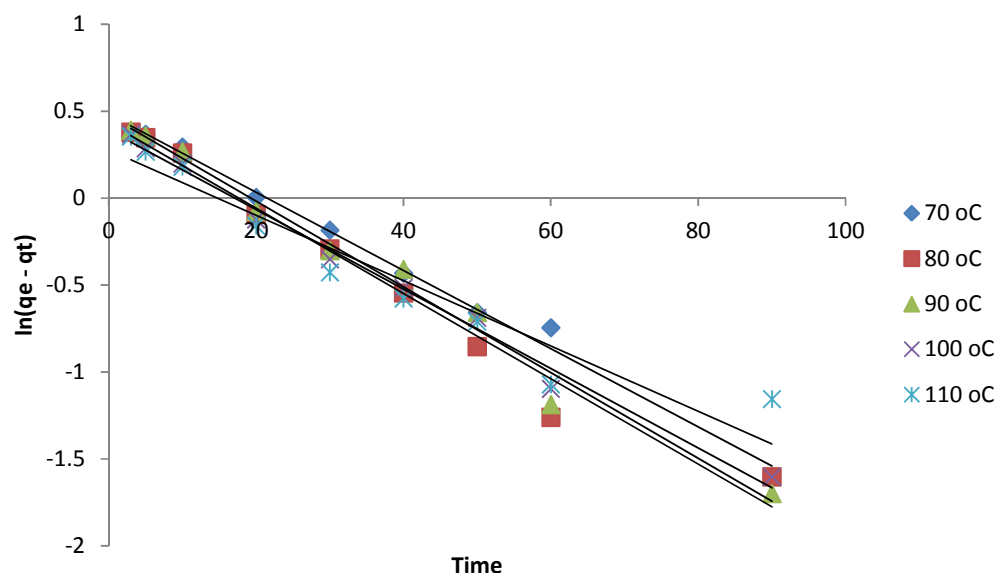


Figure 4: Pseudo First order kinetic plot

3.5.2 Pseudo-Second Order Kinetic model

The linear form of the pseudo-second order expression is:

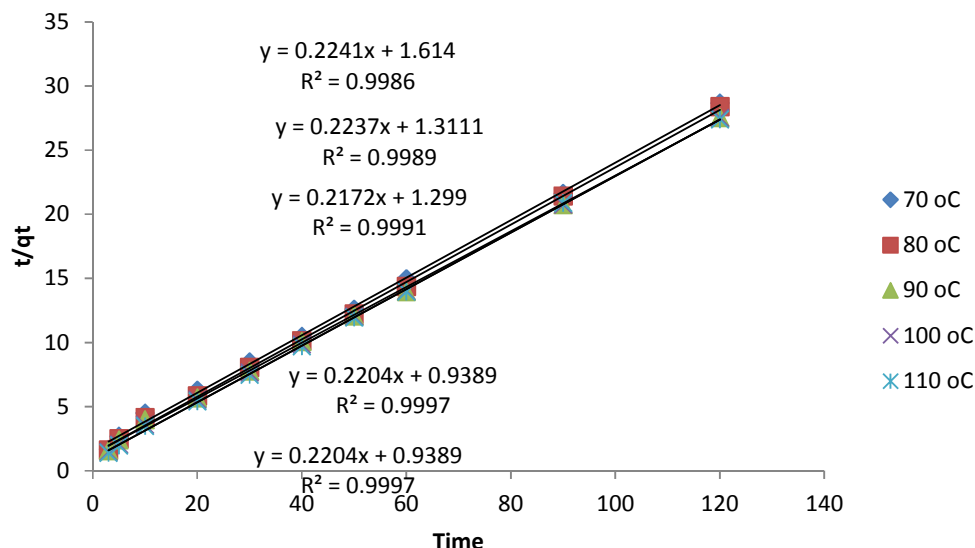
$$t/q_t = 1/K_2q_e + t(1/q_e) \quad (4)$$

Where q_e and q_t are the amounts adsorbed at equilibrium time and at any time t respectively (mg/g), K_2 is the Pseudo-second order adsorption rate constant (g/mgmin), and t is the contact time (min). The Pseudo-second order rate constant K_2 and q_e for all adsorbents at different temperatures were determined from the slope and intercept of the plot of t/q_t versus t in figure 5.

The correlation coefficient R^2 has very high values of greater than 0.99 for the adsorbent.

This suggests a very good correlation of the bleaching process with these adsorbents.

219 Equally, the values of the calculated equilibrium adsorption capacity (q_e) were very close to
 220 the experimental values. Therefore, the Pseudo-second-order model is satisfactorily
 221 applicable to the bleaching of palm oil using these adsorbents.



222

223 Figure 5:Pseudo-second order kinetic model

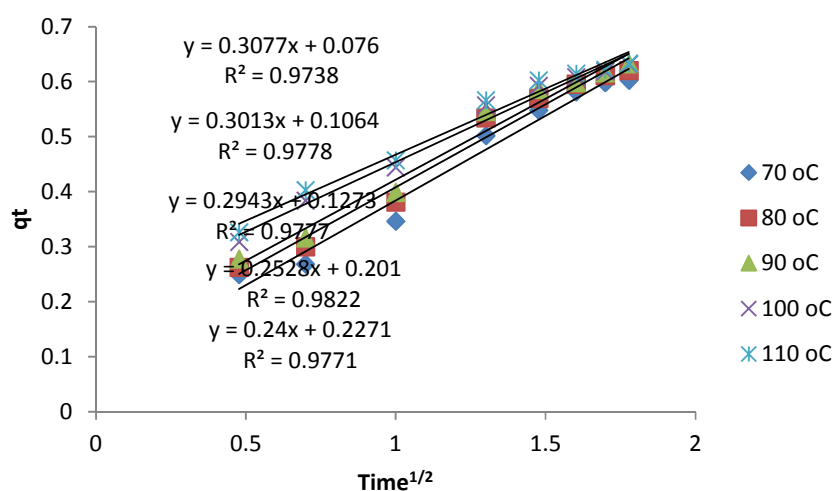
224 3.5.3 Intra-Particle Diffusion Kinetic Model

225 The most commonly used technique for identifying the mechanism involved in the adsorption
 226 process is the intra-particle diffusion plot which expresses the relationship between the
 227 adsorption capacity (q_t) at time $t^{1/2}$. The intra-particle diffusion equation is as expressed in
 228 equation 4. [17].

$$229 \quad q_t = Kt^{0.5} + \varepsilon \quad (5)$$

230 Where q_t is the amount adsorbed at time t (mg/g), K_d is the rate constant of the intra particle
 231 transport (g/mg/min), ε is the equilibrium concentration associated with boundary layer
 232 thickness (mg/l), and t is the contact time (min). The intra-particle diffusion rate constants,
 233 K_d and ε for all adsorbents at different temperatures were determined from the slope and
 234 intercept of the plot of q_t versus $t^{0.5}$.

235 If the linear plot of q_t versus $t^{1/2}$ passes through the origin, then the intra-particle diffusion
 236 will be the sole rate-limiting process [18]. The rate-limiting step is the slowest step of the
 237 process where the boundary layer of solute is adsorbed on the solid surface from the bulk of
 238 the solution in a batch process [19]. The linear lines did not pass through the origin due to the
 239 difference in mass transfer rate from the initial to the final stage of adsorption. The deviation
 240 of the linear lines from the origin indicates that intra-particle transport is not the sole rate-
 241 limiting step.



242

243 Figure 6: Intra particle diffusion kinetic model plot

244 Table 4: Calculated batch kinetic parameters for the bleaching process

Kinetic Model	Temperature °C				
	70	80	90	100	110
Pseudo-first order					
K_1	1.271	1.246	1.244	1.280	1.239
q_e	3.565	3.475	3.467	3.597	3.451
R^2	0.993	0.997	0.996	0.980	0.993
Pseudo-second order					
K_2	0.0130	0.0152	0.0186	0.0232	0.0252
q_e	6.579	6.667	6.944	7.092	7.692

R ²	0.983	0.990	0.996	0.998	0.999
Intra-particle diffusion					
K _d	2.009	2.178	2.421	2.710	3.119
A	0.229	0.222	0.217	0.205	0.194
R ²	0.978	0.993	0.993	0.983	0.973

3.6 Isotherm Studies

The adsorption isotherm is a relationship between the amount of a substance removed from the liquid phase by a unit mass of adsorbent and its concentration at a constant temperature. The adsorption isotherm is the basic requirement for designing any adsorption system [20]. Different adsorption isotherm models were used to determine the adsorption capacity of the activated Nando clay used in the bleaching of the crude palm oil and to obtain the best interpretation of the adsorption process.

3.6.1 Langmuir isotherm

The Langmuir model assumes that the uptake of the carotene molecules occurs on a homogeneous surface by monolayer adsorption [21].

The linear form

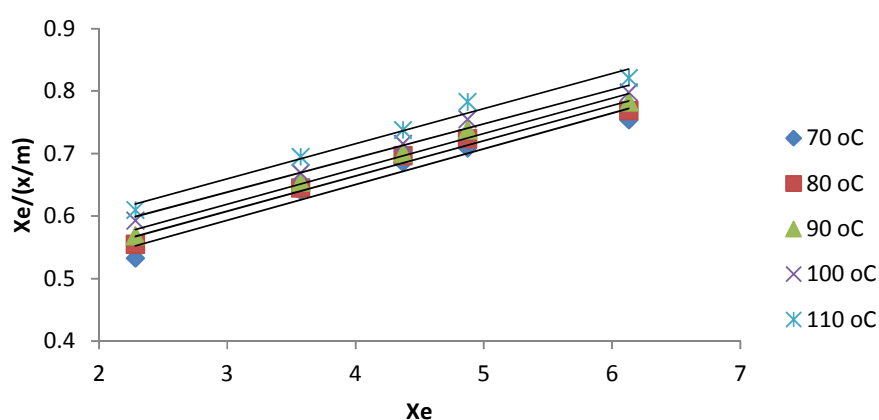
$$\frac{x_e}{x/m} = \frac{1}{a} + \frac{a}{b} X_e \quad (6)$$

For the Langmuir isotherm, the values of $X_e/(x/m)$ were plotted against X_e in figure 7 from where the Langmuir constants a and b were determined from the intercept and the slope of the linear plot and presented representing the adsorption equilibrium constant and maximum adsorption capacity respectively.

The value of “ a ” is a measure of the surface area of the clay. The high positive value of “ b ” indicates that Nando clay is good for the adsorptive bleaching of palm oil [21]. It was

265 observed that the maximum adsorption capacity of Nando clay is about 36 to 42 mg/g. The R^2
 266 values ranged from 0.957 to 0.984 for the activated Nando clay
 267 This shows that the adsorption of the carotene from the crude palm oil on the adsorbents
 268 followed Langmuir isotherm. The fact that the Langmuir isotherm fits the experimental data
 269 very well may be due to a homogeneous distribution of active sites on the activated clay.
 270 Some bleaching processes by some authors conformed to Langmuir model [6, 14].

271



272

273 Figure 7. Langmuir Isotherm for the bleaching process

274 3.6.2 Freundlich Isotherm

275 A linear form of the Freundlich isotherm is given as [23].

$$276 \quad \log x/m = \log K_f + n \log X_e \quad (7)$$

277 Where x/m is the amount of adsorbate per unit mass of adsorbent (mg/g), X_e is the solute
 278 equilibrium concentration of adsorbate (mg/l).

279 Hence, the plot of $\log x/m$ against $\log X_e$ in figure 8 was used to investigate the Freundlich
 280 isotherm. The values of the Freundlich constants K_f and n were calculated from the intercept
 281 and the slope respectively. The constant K_f is a measure of the adsorption capacity while
 282 constant n is a measure of the intensity or favorability of adsorption. For beneficial

adsorption, the value of n will be between 0 and 10 [24]. In this work, all the values of n ranged from 0.4 to 1.2 showing beneficial adsorption of the carotene from the crude palm oil. The correlation coefficient R^2 ranged from 0.956 to 0.993 indicating that the adsorption followed Freundlich isotherm model. Similar results were obtained by [16, 24]

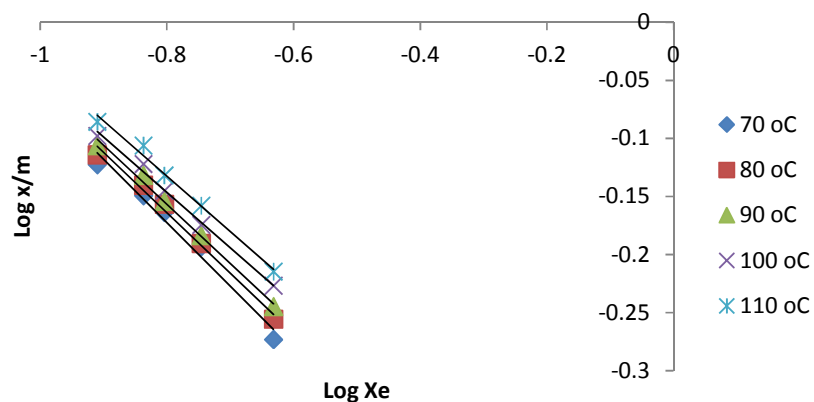


Figure 8: Freundlich Isotherm for the bleaching process

Table 5. Calculated batch isotherm parameters

Isotherm Model	Temperature °C				
	70	80	90	100	110
Langmuir					
R_L	0.00040	0.00041	0.00042	0.00043	0.00046
b	41.667	40.768	39.768	39.074	36.446
a	2.375	2.283	2.227	2.110	2.041
R^2	0.957	0.975	0.982	0.984	0.976
Freundlich					
K	0.246	0.264	0.274	0.297	0.307
$-n$	0.546	0.519	0.508	0.476	0.476
R^2	0.976	0.990	0.993	0.993	0.989

3.7 Thermodynamics Study

Thermodynamics properties were evaluated using parameters such as free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0). ΔG^0 determines if the process is feasible and spontaneous or not, ΔH^0 determines if the process is exothermic or endothermic, and ΔS^0 determines the increase or decrease in the randomness of the process at the solid/solution interface. Reactions occur spontaneously at a given temperature if ΔG^0 is a negative quantity [25]

By plotting $\ln K_L$ against $1/T$ (absolute temperature) in figure 9, quantities ΔH and ΔS were calculated from the slope and intercept respectively.

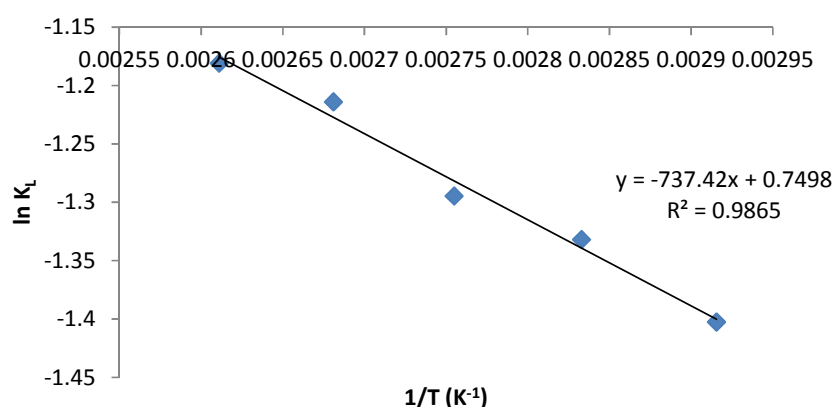


Figure 9: Thermodynamics plot for the bleaching of palm oil

The values of ΔS were positive suggesting favorable increased randomness. This is because the number of water molecules surrounding the adsorbate decreased during the adsorptive bleaching process and thus, the degree of freedom of the water molecules increased indicating that the degree of randomness at the solid-solution interface of the adsorption increased [16]. The adsorbed solvent molecules which were displaced by the adsorbate species gain more transitional entropy than is lost by the adsorbate ions/molecules, thus allowing for the prevalence of randomness in the system [14].

The positive values of ΔH indicate the endothermic nature of the bleaching process. This implies that more heat is needed as the reaction proceeds. The adsorption process in the solid-liquid system is a combination of two processes namely: the desorption of the solvent, molecules that have been adsorbed and the adsorption of the adsorbate species. In an endothermic process, the total energy adsorbed in bond breaking is more than the total energy released in the bond making between the adsorbate and the adsorbent. Hence, more energy is needed as the process progresses.

The ΔG° was negative indicating that the bleaching process is spontaneous at that high temperature used. The values of ΔG° were approximately constant though with a slight increase as the temperature increases. A decrease in the negative values of ΔG° with an increase in temperature indicates that the adsorption process is more favorable at high temperatures [14].

Table 6: Thermodynamics parameters for the adsorbents

Temp (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS (KJ/mol)
343	- 3.999	6.127	3.982
353	-3.909		
363	-3.907		
373	-3.764		
383	-3.760		

3.8 Activation Energy

The linear form of the Arrhenius equation was used to determine the activation energy of the adsorption process

$$\ln K = \ln A - \frac{E_a}{RT} \quad (8)$$

where K is the pseudo-second-order rate constant (g/mol min), A is the frequency factor (g/mol min), T is the absolute temperature (K), R is the gas constant (8.314 J/mol K) and E_a is the activation energy (KJ/mol).

The activation energy for Nando clay bleaching was 15.281 KJ. Generally, the activation energy for the process is high suggesting that much energy is required to initiate or start the bleaching process.

4. CONCLUSION

The use of low cost adsorbent developed from Nando clay in adsorptive bleaching of palm oil was studied in this work. Acid activation method was used in preparing the clay. Adsorbent dosage, temperature and particle size was found to affect the bleaching efficiency. The equilibrium data were well described by the Langmuir and Freundlich kinetic models. Both the pseudo-first-order and the pseudo-second-order kinetic models describe efficiently the experimental data of the bleaching process. The equilibrium data were described better by Langmuir and Freundlich models for the adsorptive bleaching of palm oil. The enthalpy, entropy and activation energy were determined to be 6.127KJ/mol, 3.982KJ/mol and 15.281KJ respectively. The free energy was found to vary between -3.999 to -3.760KJ/mol. The result indicates that bleaching efficiency of up to 96% can be obtained with the activated clay as an adsorbent.

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