

# Adsorption Isotherm and Thermodynamic Studies of the Bleaching of Palm Oil using Modified Shells Powder

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## Abstract

The use of locally sourced materials as adsorbents has been investigated as a result of high cost of bleaching clay for the purpose of bleaching vegetable oils. Consequently, shells such as oyster and periwinkle as wastes were collected and processed into powder forms (oyster shell powder; OSP and periwinkle shell powder; PSP) and used for the removal of colour pigments and other minor impurities from palm oil. Adsorption studies were carried out at different temperatures (308, 328, 348, 368, and 388 K) and adsorbent dosages (1.0, 1.5, 2.0, 2.5, 3.0 g). The equilibrium adsorption data were tested with three isotherms: Langmuir, Freundlich, and Dubinin-Radushkevich (D-R). Best fit was found to be Freundlich isotherm with its range of correlation coefficient  $R^2$  of (0.955 to 0.966). The negative values of  $\Delta G^\circ$  showed that the adsorption process is feasible and spontaneous and the negative values of  $\Delta H^\circ$  suggested exothermic nature of the adsorption process while the positive and low values of  $\Delta S^\circ$  indicated good affinity between the adsorbents and the adsorbate. The values of mean free energy (E kJ/mol) obtained from Dubinin-Radushkevich which was less than 8 kJ/mol and the values of  $\Delta H^\circ$  which were less than 20 kJ/mol suggested the adsorption process to be physisorption.

**Keywords:** Isotherms, Adsorption, Powder Oyster and Periwinkle shells, Palm oil.

## 1. INTRODUCTION

Fats and oils are the raw materials used for production of liquid oils, shortenings, margarines, and other products. Humans have used fats and oils for food and a variety of other applications from time immemorial as the oils can be isolated easily from their source. These ingredients were found to improve on the flavour, and add satiety to foods. The highest energy source of the three basic foods (carbohydrates, proteins, and fats) are found in fats and oils and many contain fatty acids essential for human health that are not manufactured by the human system. Fats and oils occur naturally in a wide range of sources, with each source providing a separate and distinctive material. Hundreds of seeds and fruits bear oil, all animals produce fat, and marine sources also provide oils. All edible fats and oils are water insoluble substances that consist predominantly of glycerol esters of fatty acids, or triacylglycerol, with some non saponifiable matter present in trace quantities. The terms fats and oils are used interchangeably, and the choice of terms is usually based on the physical state of the material at ambient temperature. Generally, fats appear solid at ambient temperatures and oils appear liquid but it is

the chemical composition that defines the characteristics of the individual fat or oil, which in turn determines the suitability of this ingredient in various processes and applications.

The oil palm (*Elaeis guineensis*) produces two distinct oils; palm oil and palm kernel oil. It grows in the tropical regions of Asia, Africa, and America and predominantly in Nigeria, Malaysia and Indonesia (Jalani et al., 2000). Palm oil is derived from the mesocarp of the palm fruit, species *Elaeis guineensis*. Presently, palm oil is the second largest vegetable oil in the world production and the leader in the world exports (Pantzaris, 1995). In general, palm oil had reddish brown in colour due to its high content of carotenoid;  $\alpha$  and  $\beta$  carotene about 500-700 ppm. The chain length of fatty acids present in the triglyceride has a very narrow range from 12 to 20 carbon atoms (Basion 1996).

Bleaching is an adsorption process whereby clay is used as adsorbent. It is used in vegetable oil refinery industries to stabilize the oil by removing coloured and colourless pigments that destabilize vegetable oils (Didi et al., 2009; Usman et al., 2013).

Refining process of crude vegetable oils involves several stages such as degumming, neutralization, bleaching and deodorization (Al-Zahrani *et al.*, 2000; Berbesi, 2006, CIWC, 2008, Farihahusnah *et al.*, 2011; Adel Abd EL-Razek *et al.*, 2017). Bleaching is the most critical stage since it helps to enhance the quality and improve the appearance, flavour, taste and stability of the final oil products (Farihahusnah *et al.*, 2011; Rohani *et al.*, 2006). The bleaching process is carried out after degumming and neutralizing the vegetable oil under specific conditions (Diaz and Santos, 2001).

Activated bleaching clay is the most common adsorbent used for oil purification. Other adsorbents that have been tested for adsorption of colour pigments and other impurities from oil included activated carbon and silica based products (Ejikeme *et al.*, 2013). Bentonite clays are used widely as binding agent in foundry sand and iron ore palleterization. Acid activated clays have been used as catalysts in industrial processes (Foletto *et al.*, 2011; Didi *et al.*, 2009, EUBA, 2011). The application of activated clays in paper industry have also been reported, production of sulphur for environmental protection (Foletto *et al.*, 2011, EUBA, 2011). Activated carbon has the potentials in the removal of colour pigments, odours, tastes and contaminants in vegetable oils and in water purification processes (Lin and Zhao. 2016). However, synthetic activated carbons usually prepared from petroleum sources are expensive and non-biodegradable and therefore pose serious threat of environmental pollution after use (Abba *et al.*, 2018).

Acid activation of clay has been investigated to effectively improve the adsorption property of clay (Foletto *et al.*, 2011). Clays in their activated forms are extensively used in the fat and oil industries in the bleaching of vegetable oils. Imported bleaching clays make oil production expensive yet local materials can be used if properly prepared (Mukasa-Tebandek *et al.*, 2016).

Generally, the demand for edible oil is continuously increasing. Thus, there is need to initiate the development of raw materials that can serve as alternative to clays. The commercial bleaching earth used is for the most part imported by the refining industries. Therefore, it is important to investigate the use of non-clay materials for their potential in making substitutes for this purpose since the materials are cost effective and readily available compare to the imported and expensive clays

## 2. EXPERIMENTAL

### Materials and methods

Palm oil (PO) was bought from the production site in Auchi, Edo state, Nigeria while oyster and periwinkle shells were purchased in Warri, Delta state, Nigeria. All chemicals used were of reagent grade.

### Activation of Oyster shell powder (OSP)

OSP was prepared by washing the oyster shells with hot water to remove surface dirt, sun dried, crushed and ground to powder form using a roller mill machine and sieved using a sieve of 100  $\mu$ . The particle size was activated with 5 M HCl. The reagent (100 mL) was added to 250 g of OSP, heated in a water bath at 80 °C for 30 min. The mixture was washed severally with distilled water in order to remove the residual activating reagents and then filtered, dried in an electric oven at 105 °C for two hours. The dried sample was ground and sieved again to required particle size (100  $\mu$ ) and stored in a clean dry container for the purpose of bleaching the PO. The same procedure was repeated for periwinkle shell powder (PSP).

### Pretreatment of the Oils

#### Degumming

The oil was initially heated up to 60 °C in order to melt the oil before treatment with a food grade phosphoric acid (approximately 85 %) about 0.1 % of oil weight was thoroughly mixed and stirred for about 10 – 15 min to decompose the non-hydratable phosphatides present in the oil as well as to coagulate the phosphatides making them insoluble and for easy adsorption during bleaching.

### Bleaching and Adsorption Studies

#### The bleaching of palm oil and adsorption process

The bleaching experiments were performed by batch method on a thermostatically controlled hot plate with stirrer. The degummed oil (50 g) was treated with 1.0 g of activated adsorbent separately at varied temperatures of 308, 328, 348, 368, and 388 K for 30 min. The hot mixture was then filtered using a filter paper. During the measurement of the absorbance, the filtered oil (2.5 g) was transferred into 25 mL standard flask and diluted and make up to the mark with n-hexane (w/v). The bleaching efficiency of the adsorbent was determined by measuring the colour of bleached oil using a UV-Vis spectrophotometer at wavelength of 450 nm. The same procedure was repeated for 1.5, 2.0, 2.5 and 3.0 g. of activated adsorbent.

The percentage bleaching efficiency of the oyster shell powder was determined as:

$$\% \text{ bleaching efficiency} = \frac{A_o - A_t}{A_o} \times 100 \dots \dots \dots (1)$$

where;  $A_o$  and  $A_t$  are the absorbances of the unbleached and bleached oil samples respectively.

### Adsorbents Characterization: Analysis using Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)

Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS) brand instrument was used to observe the surface of cells or other microscopic structures that is surface morphology of the samples. The elemental compositions of untreated and treated adsorbents were determined using energy dispersive spectroscopy.

## 3. RESULTS AND DISCUSSION

### Elemental composition of adsorbents

Presented in Table 1 are the elemental compositions of activated and unactivated oyster shell, periwinkle shell. The reduction in the CaO content indicated that the  $Ca^{2+}$  exchange cations were replaced by hydrogen ions and polyvalent cations leached from the octahedral sheet.

**Table 1: Elemental Composition of Treated and Untreated Adsorbents**

	OSP		PSP	
	Un-treated	Treated	Un-treated	Treated
MgO	0.80	0.69	1.00	0.52
Al <sub>2</sub> O <sub>3</sub>	2.87	0.95	0.79	0.40
SiO <sub>2</sub>	0.77	0.68	1.11	16.2
CaO	77.9	35.7	56.2	48.7
Na <sub>2</sub> O	0.70	0.62	1.10	0.78
Fe <sub>2</sub> O <sub>3</sub>	13.8	4.30	9.29	BDL

The decrease in the octahedral sheet oxides; Al<sub>2</sub>O<sub>3</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub> along with the increase in silica content proved that the original structure was altered. The behavior shown by these oxides contents with acid modification is related to the progressive dissolution

of the adsorbents minerals. The destruction of the octahedral layer leached the cations into solution, while the silica generated by the tetrahedral layer remains in the solid phase due to its insolubility (Diaz *et al.*, 2003).

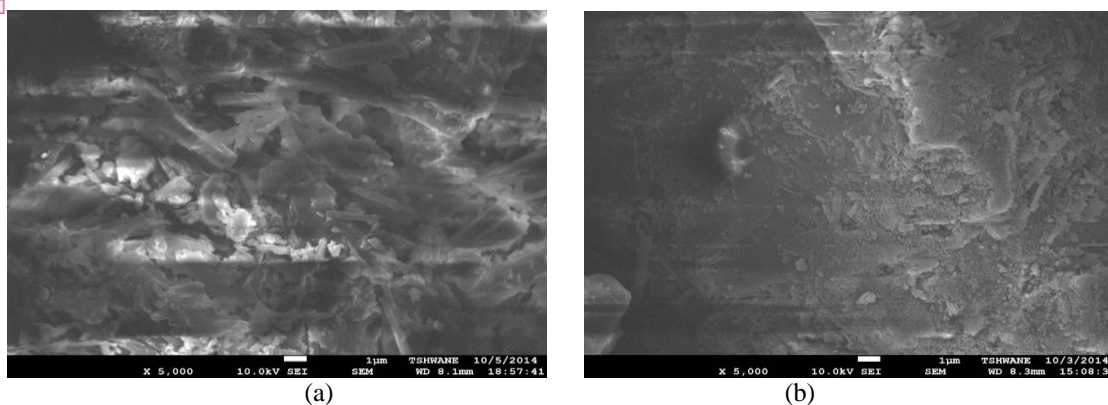
The increase in relative content of these cations occurs as a result of depletion of the cations from the interlayer and octahedral sheets of the samples structures. Pesguera *et al.*, (1992) suggested that this free silica generated as a result of initial destruction of the tetrahedral layer was polymerized by the effect of activating reagents and was deposited on the undestroyed silicate layers protecting it from any further attack by the reagents. The silica content showed increase in periwinkle shell powder modified with 5 M HCl.

The decrease in the amount of other oxides was due to the dissolution of the adsorbents minerals as a result of modification by acid. The lower value of Fe<sub>2</sub>O<sub>3</sub> and its absence in some of the adsorbent samples after modification proved them to be efficient for the adsorption process (Egbuna *et al.*, 2014), This results in the creation of more pore size and volume which enhanced the adsorption capacity of the activated adsorbent samples. The tetrahedral cations are generally the most resistant to acid attack, followed by the octahedral cations with exchangeable cations the most vulnerable.

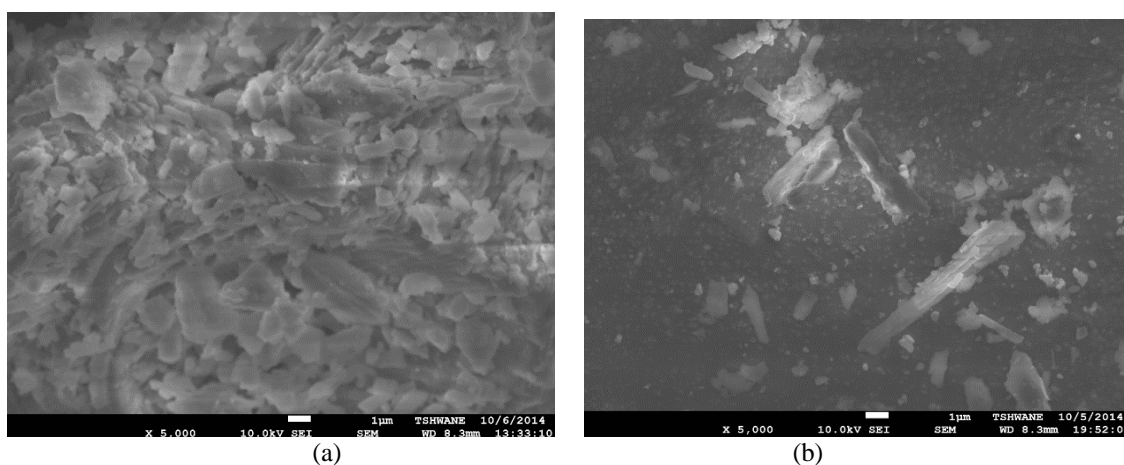
However, a considerable amount of these elements is still found in the activated samples due to the presence of impurities which is due to feldspar that has calcium, and sodium that is resistant to acid attack and precipitated as a new amorphous phase from the leachate.

### Scanning electron microscopy (SEM) analysis

Presented in Figures 1 and 2 are the scanning electron micrographs of oyster shell and periwinkle shell respectively. The SEM micrographs were studied for the surface and morphological characteristics in the adsorbent materials. In comparison with the unmodified OSP, the SEM images showed clear changes in the micrographs of all the modified adsorbent materials in comparison to the unmodified adsorbents. This change in the SEM micrographs revealed the structural changes in the modified adsorbent materials.



**Figure 1:** Scanning electron micrographs of untreated (a) and (b) HCl-treated Oyster shell powder.



**Figure 2:** Scanning electron micrographs of (a) untreated and (b) HCl-treated Periwinkle shell powder.

The modified adsorbents looked more porous than the unmodified. Figure 1b appeared smooth on the surface with thread-like structure in nature when compared with the untreated oyster shell powder which indicates that impurities have been removed from the adsorbent after activation. Figure 2a was the untreated periwinkle shell powder which looked like flakes and PSP treated with 5 M HCl (Figure 2b) appeared like broken rod particles due to creation of more pores and increase in pore volumes.

#### Effect of adsorbent dosage.

The adsorbents (oyster shell and periwinkle shell powder) were varied from 1.0 to 3.0 g in 50 g of palm oil. The relative bleachability is shown in fig 3 at 368 K optimum bleaching temperature. The quantity of activated bleaching adsorbents required for the bleaching of vegetable oil depends on the quality of the oil, activity of the adsorbents and process conditions (Hoffmann, 1989).

It was observed that increasing the adsorbents dosage increased the bleaching efficiency in OSP

treated with 5 M HCl. The results are in agreement with those obtained by Kheok and Lim (1982) who reported that an increase in clay dosage would be expected to lead to an increase in colour reduction. This can be attributed to the increase in the number of adsorption sites as a result of the increase in surface area, pore sizes, and volumes of the adsorbents as dosage increases. The percentage bleaching efficiency decreased using 2 g of the adsorbent (PSP) with 5 M HCl while it further increase when the quantity of adsorbent was increase from 2.5 to 3.0 g. This might be as a result of equality in the rate of adsorption and desorption whereby most of the adsorbed materials dissolve back into the oil due to high temperature that convert the pigments to colourless form. It is observed that the activated OSP and PSP perform better than the unmodified ones.

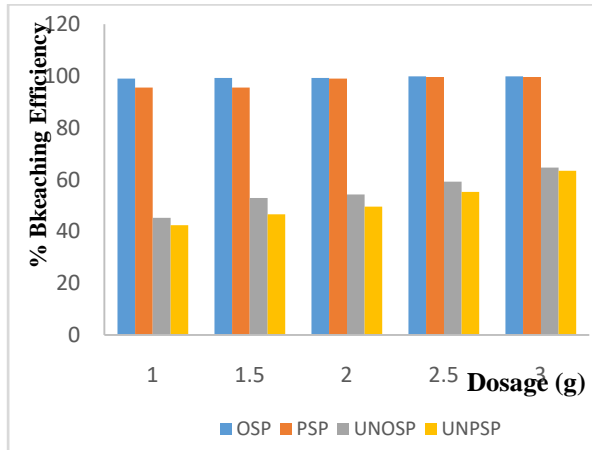
#### Effect of Bleaching Temperature

The bleaching efficiency was determined by varying the contact temperature in the range 308 to 388 K by keeping the other parameters constant. The



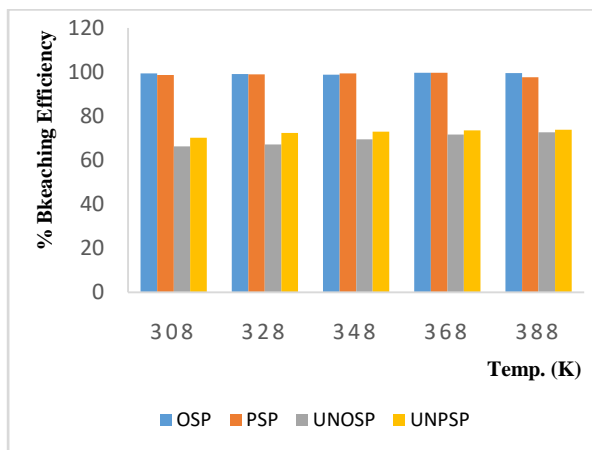
adsorption equilibrium was attained at 308 K using OSP treated with 5 M HCl as presented in Figure 4 using 3 g optimum adsorbent dosage.

The increase observed at 348 to 368 K was due to the rate of adsorption equal the rate of desorption whereby some of the adsorbed pigments dissolved back into the oil and converted into colourless forms after equilibrium has been achieved. This was attri-



**Figure 3.** Bleachability of OSP and PSP with palm oil showing the effect of dosage

uted to heat bleaching effect at high temperature (Madya *et al.*, 2006). However, percentage bleaching efficiency increase in PSP treated 5 M HCl up to 368 K this caused the amount of colour pigments adsorbed to increase and consequently the residual relative amount in palm oil phase decreased which seems to support the assertion that higher temperature create more adsorption sites in the adsorbent phase (Sabah *et al.*, 2005).



**Figure 4:** Bleachability of OSP and PSP with palm oil showing the effect of temperature

The graph shows that activated adsorbents displayed better efficiency in comparison with the

unmodified OSP and PSP in the bleaching of palm oil.

### Adsorption Isotherms: Langmuir isotherm model

The Langmuir isotherm has been employed to explain the adsorption of oil pigment and other minor oil solutes during oil processing. Though, developed by Irving Langmuir in 1916 to describe gas adsorption. The model assumes that the adsorbate is bound to a fixed number of energetically equal, specific sites, each adsorbing one molecule with no interaction occurring between molecules on adjacent sites (Proctor *et al.*, 2005). The Langmuir isotherm has been applied to pigment adsorption from vegetable oil in the form written according to Equation 2:

$$\frac{x_e}{x/m} = \frac{1}{ab} + \frac{1}{a}x_e \quad (2)$$

where  $x$  = amount of solute adsorbed in PO,  $X_e$  = amount of unadsorbed solute in PO,  $m$  = grams of adsorbent used, 'a' is the surface area of the adsorbent ( $m^2/100g$ ), and  $b$  is a constant of the intensity of the adsorption. According to general belief, adsorption of the colour bodies from a solution or dispersion is predominantly a surface phenomenon and is dependent upon the specific affinity between adsorbent and solute. The solute may be either dissolved or colloiddally dispersed. The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant of separation factor or equilibrium parameter,  $R_L$  which is defined by Equation 3

$$R_L = \frac{1}{1 + bC_o} \dots \dots \dots (3)$$

where,  $b$  (L/mg) is the Langmuir constant,  $C_o$  is the highest initial concentration (mg/l). The  $R_L$  values indicate the shape of the isotherm.  $R_L$  values between 0 and 1 indicate favourable adsorption; while  $R_L \geq 1$  indicate unfavourable and  $R_L$  equal 0 is irreversible adsorption.

### Freundlich isotherm model

Freundlich in 1926 developed an empirical equation that correlates the capacity of the adsorbent with the residual solute concentration.

$$\frac{x}{m} = kc^n \dots \dots \dots (4)$$

where  $x$  = amount of solute adsorbed (mg),  $m$  = amount of adsorbent (g),  $c$  = amount of residual solute (concentration) (mg/L) at equilibrium. The

Freundlich model is used to estimate the adsorption affinity of the sorbents towards the adsorbate.  $K$  is a constant indicating adsorption capacity, and  $n$  is a constant of the energy of adsorption. Empirical data are evaluated for Freundlich behavior by using the equation in its logarithmic form, as equation of a straight line (Achife *et al.*, 1989).

$$\log \frac{x}{m} = \log k + n \log x_e \dots \dots \dots (5)$$

**Dubinin- Radushkevich isotherm model**

Dubinin – Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Dabrowski, 2001; Gunay *et al.*, 2007). The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.

$$q_e = (q_s) \exp(-K_{ad} \varepsilon^2) \dots \dots \dots (6)$$

$$\ln q_e = \ln(q_s) - (K_{ad} \cdot \varepsilon^2) \dots \dots \dots (7)$$

$q_e$  = amount of adsorbate in the adsorbent at equilibrium(mg/g);  $q_s$  = theoretical isotherm saturation capacity(mg/g);  $K_{ad}$  = Dubinin-Radushkevich isotherm constant ( $\text{mol}^2/\text{kJ}^2$ );  $\varepsilon$  = Dubinin – Radushkevich isotherm constant.

The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy ( $E$  kJ/mol) for removing a molecule from its location in the sorption space to the infinity, which can be computed by the relationship (Dubinin, 1960 and Hobson, 1969).

$$E = \left( \frac{1}{\sqrt{2} B_{DR}} \right) \dots \dots \dots (8)$$

$B_{DR}$  is the isotherm constant

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \dots \dots \dots$$

where  $R=8.314$  J/mol.K;  $T$ =absolute temperature;  $C_e$  = adsorbate equilibrium concentration (mg/L). One of the unique features of the Dubinin – Radushkevich ( D-R) isotherm model lies on the fact that it is temperature – dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed  $\ln q_e$  against  $\varepsilon^2$  the square of potential energy. All suitable data will lie on the same curve, named as the characteristic curve (Foo *et al.*, 2010). The constant such as  $q_s$  and  $K_{ad}$  are determined from the appropriate plot using Equation 7

The adsorption isotherm models constants and the correlation coefficient ( $R^2$ ) as obtained from the slope and intercept of graphs in figures 5 to 7 are reported in Tables 2, 4 and 5 respectively. The Langmuir isotherm maximum adsorption ( $q_m$ ) (Table 2) in OSP is better than in PSP. The  $R_L$  values for OSP and PSP are presented in Table 3. The  $R_L$  values at varied temperatures are between 0 and 1 indicating favourable adsorption for both adsorbents. Then (the adsorption intensity) values observed in Freundlich isotherm (Table 4) shows that the values were less than 1 an indication of favourable adsorption while the adsorption capacity ( $K$  mg/g) was better in OSP due to higher values obtained an indication of better bleaching efficiency. The correlation coefficients ( $R^2$ ) as calculated shows that they are all conformed except in D-R (OSP) at 328 K ( $R^2 = 0.11$ ).

Despite the fact that the value of  $R^2$  in D-R isotherm (Table 5) is 1.00 in PSP at 328 K which showed the highest linearity in the adsorption process but the range of the correlation coefficient  $R^2$  (0.955 to 0.966) in Freundlich isotherm using PSP show better conformity than D-R isotherm follow by Langmuir isotherm (0.876 to 0.945) in PSP. The mean free energy  $E$  (kJ/mol) which is defined as the free energy change when one mole of ion is transferred to the surface of the solid, the values are listed in Table 5. The values are less than 8 kJ/mol shows that the adsorption is physisorption.

**Table 2:** Langmuir Isotherm

Temp. K	OSP			PSP		
	$q_m$ (mg/g)	$b$ (L/mg)	$R^2$	$q_m$ (mg/g)	$b$ (L/mg)	$R^2$
308	0.2562	28.71	0.920	0.0613	602.10	0.876
328	0.0998	221.46	0.756	0.0308	2435.21	0.928
348	0.0301	2566.9	0.827	0.0299	2604.48	0.939
368	0.0268	3248.63	0.903	0.0372	1671.57	0.942
388	0.0271	3189.98	0.782	0.0293	2686.03	0.945

**Thermodynamic Studies**

Thermodynamic study of adsorption process is essential to conclude whether the process is spontaneous or not. The thermodynamic parameters considered in this study are change in Gibb’s free energy ( $\Delta G^0$ ) change in enthalpy ( $\Delta H^0$ ), change in entropy ( $\Delta S$ ). They have useful role to determine

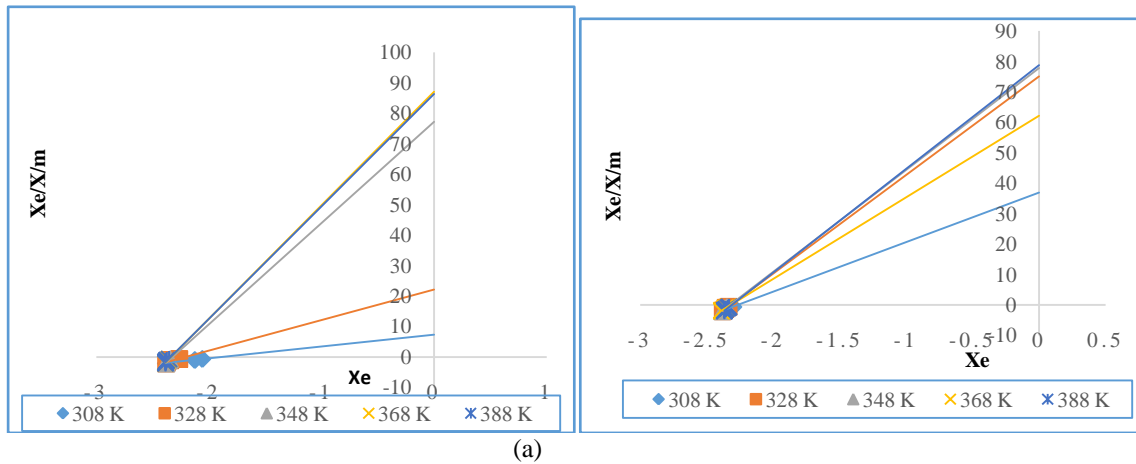


Figure 5. Langmuir isotherms of OSP treated with (a) HCl and PSP treated with (b) HCl

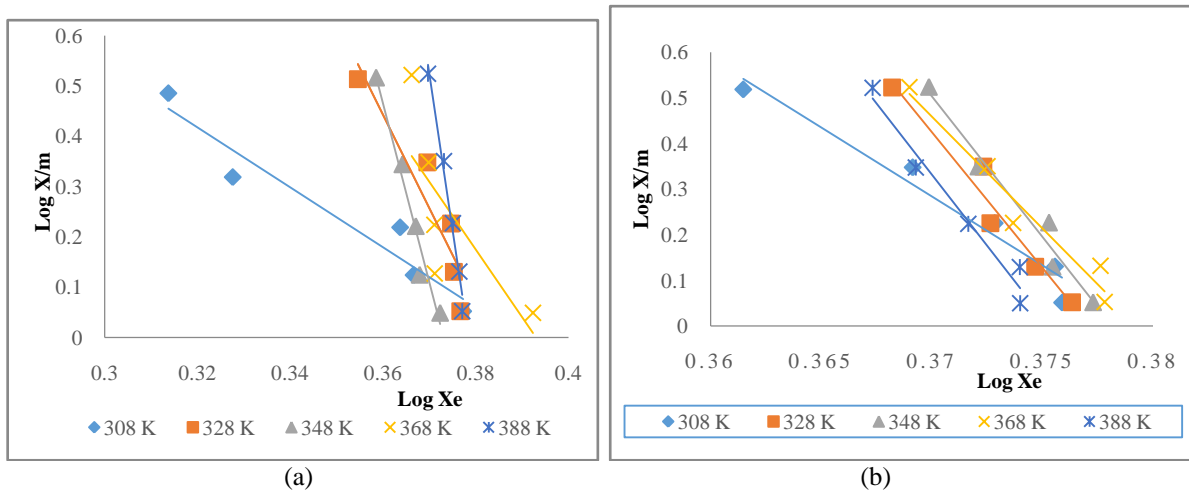


Figure 6: Freundlich isotherms of OSP treated with (a) HCl and PSP treated with (b) HCl

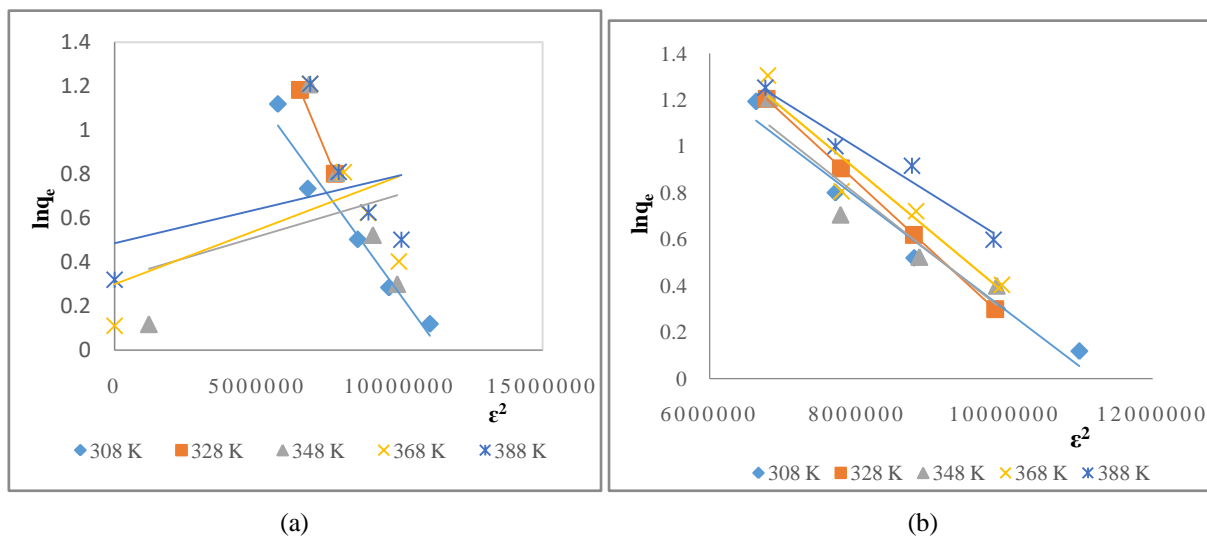


Figure 7: D-R isotherms of OSP treated with (a) HCl and PSP treated with (b) HCl

spontaneity and heat change of the adsorption process. The modified Van't Hoff equation used to

determine the value of the equilibrium constant with temperature changes is given in Equation 10.

$$\ln X_e = \frac{\Delta S^\circ}{R} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) \dots \dots \dots (10)$$

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be obtained from the slope and intercept of the graph by plotting  $\ln K$  against  $\frac{1}{T}$ .

**Adsorption Isotherm Constants**

**Table 3:** The  $R_L$  Values for Pigments Adsorption from Palm Oil Onto Activated OSP and PSP

Temp (K)	OSP	PSP
308	0.01017	0.00049
328	0.00133	0.000121
348	0.000115	1.13E-04
368	9.08E-05	0.000176
388	9.25E-05	0.00011

**Table 4:** Freundlich Isotherm

Temp. K	OSP			PSP		
	n	k (mg/g)	R <sup>2</sup>	n	k (mg/g)	R <sup>2</sup>
308	-5.96	2.732	0.927	-30.22	0.944	0.956
328	-18.59	1.172	0.862	-59.59	0.739	0.955
348	-35.56	0.891	0.964	-61.69	0.731	0.967
368	-13.44	1.384	0.559	-49.02	0.788	0.957
388	-61.98	0.729	0.983	-62.37	0.730	0.966

The Gibb's free energy can be calculated from the relationship presented in Equation 11

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \dots \dots \dots (11)$$

The calculated values of the thermodynamic parameters are listed in the table 6. The negative values of enthalpy change,  $\Delta H^\circ$  implies the exothermic nature of the adsorption process and also shows that the adsorption is physisorption since the values are less than 20 kJ/mol. The positive values of  $\Delta S^\circ$  shows increase in the randomness of the adsorption process an indication of favourable adsorption whereby the transition state is highly disordered compared to the ground state, the translational, rotational and vibrational degrees of freedom are liberated on going from the ground state to the transition state and the reaction proceeds fast and reach completion. The negative values of  $\Delta G^\circ$  confirmed the feasibility of the process and the spontaneous nature of the adsorption process.

**Activation Energy Determination**

The sticking probability,  $S^*$  of an adsorbate on adsorbent can be expressed by a modified Arrhenius-type equation related to surface coverage ( $\theta$ ). The  $S^*$  is a function of the adsorbate/adsorbent system is the

measure of the ability of an adsorbate to remain on the adsorbent indefinitely, and it is expressed as:

$$S^* = (1 - \theta) \exp - \left( \frac{E_a}{RT} \right) \dots \dots \dots (12)$$

$$\log(1 - \theta) = \log S^* + \frac{E_a}{RT} \dots \dots \dots (13)$$

where;  $\theta$  is surface coverage,  $E_a$  is activation energy.

$$\theta = \left( 1 - \frac{C_e}{C_o} \right) \dots \dots \dots (14)$$

where  $C_o$  and  $C_e$  are the initial and equilibrium concentrations respectively.

The values of  $E_a$  and  $S^*$  can be obtained from the slope and intercept of the graph of  $\log(1 - \theta)$  against  $\frac{1}{T}$ .

The values obtained for activation energy are listed in Table 6. The values are low and below 20 kJ/mol. which shows that the adsorption process is physisorption in nature and  $S^*$  which is the probability of the adsorbate to stick onto the surface of the adsorbent is below 1 an indication of high probability of the adsorbate to stick to the surface of the adsorbent (Horsfall and Spiff, 2005).

**Table 5:** Dubinin – Radushkevich

Temp (K)	OSP			E kJ/mol	PSP		
	K <sub>ad</sub> mol <sup>2</sup> /kJ <sup>2</sup>	q <sub>s</sub> mg/g	R <sup>2</sup>		K <sub>ad</sub> mol <sup>2</sup> /kJ <sup>2</sup>	q <sub>s</sub> mg/g	R <sup>2</sup>



308	2.00E-07	3.22	0.961	1.58	2.00E-07	2.31	0.972	1.58
328	4.00E-07	2.19	0.11	1.12	3.00E-07	1.99	1.000	1.29
348	3.00E-07	2.05	0.979	1.29	3.00E-07	2.24	0.883	1.29
368	5.00E-08	1.91	0.217	3.16	3.00E-07	2.09	0.925	1.29
388	3.00E-08	3.19	0.129	4.08	2.00E-07	2.42	0.961	1.58

**Table 6:** Thermodynamics Parameters

Temp (°C)	OSP				PSP						
	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)	$\Delta G$ (kJ/mol)	$E_a$ (kJ/mol)	$S^*$	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)	$\Delta G$ (kJ/mol)	$E_a$ (kJ/mol)	$S^*$	
308	-14.16	0.0431	-25.92	0.929	-1.198	-0.413	0.0083	-2.677	0.179	-0.987	
328	-0.59	0.0088	-2.991	0.256	-0.869	-0.215	0.0078	-2.333	0.093	-1.107	
348	-0.19	0.0077	-2.292	0.834	-1.042	-0.21	0.0077	-2.322	0.091	-1.105	
368	-0.18	0.0077	-2.289	0.357	-0.649	-0.262	0.0079	-2.425	0.114	-1.071	
388	-0.16	0.0076	-2.254	0.107	-1.072	-0.209	0.0077	-2.313	0.090	-1.118	

#### 4. CONCLUSION

The results obtained showed that the efficiency of HCl activated OSP, PSP, for the removal of colour pigments and other minor impurities from palm oil is feasible. The findings suggest that the adsorbents (PSP) treated with 5 M HCl displayed higher percentage bleaching efficiency (99.68) at 368 K while the experimental data conform to Freundlich isotherm follow by Langmuir isotherm in PSP. The thermodynamic studies indicate the process to be spontaneous and feasible as a result of the negative values of change in Gibb's free energy ( $\Delta G^\circ$ )

#### REFERENCES

- Achife, J. and Ibemesi, J (1989). "Applicability of Freundlich and Langmuir Adsorption Isotherms in Bleaching of Rubber and Melon Seed Oils". Journal of the American Oil Chemists' Society, 66:247-252.
- Abba, C; Abdoul, W; Gaston, Z; Abdoul, N.R; Devine, B. N (2018). Bleaching of Neutral Cotton Seed Oil using Organic Activated Carbon in a Batch System: Kinetics and Adsorption Isotherms. Processes. 6:22
- Adel Abd EL-Razek Mohdaly, Khaled Abd EL-Hameed Seliem; Abd EL-Moneam Maher Abu EL-Hassan, Awad Abdel Tawab Mahmoud (2017). Effect of Refining Process on the Quality Characteristics of Soybean and Cottonseed Oils. Int. J. Curr. Microbiol. App. Sci 6(1):207-222
- Al-zahrani, A.A., Al-shahrani S.S., Al-Tawil Y.A, (2000), "Study on the activation of Soudi bentonite, part II: Characterization of the produced active clay and its test as an adsorption agent", Engineering Science. 13(2): 193-203.
- Basim, A (2011). "Rheology of Sodium and Calcium Bentonite water Dispersions: effect of electrolytes and aging time". International Journal of Mineral Processing, 98:208-213
- Basiron, Y (1996). Palm oil, In: HM YH, editor. Bailey's industrial oil and fats products. Vol 2. New York: John Wiley and Sons. 271 -375.
- Berbesi R (2006), "Achieving Optimal Bleaching Performance", Oil Mill Gazetteer, 112, 2-6.
- Crown Iron Works Company (CIWC), (2008), Oils and refining. A CPM Company. 35-47.
- Dabrowski, A (2001). "Adsorption- from theory to practice". Adv. Colloid Interface Sci. 93:135-224.
- Diaz, M. I, Suariz, M. B, Prates, S, Marhnpozas, J.M (2003). "Characterization and acid activation of Portuguese Special Clays". Clay minerals. 38:537-549
- Diaz F.V. and de Souza S.P., (2001) "Studies on the Acid Activation of Brazilian Smectitic Clays". Quim Nova, 24(3):345-353
- Didi M.A, Makhoukhi B., Azzouz A., and Villemin D (2009), "Colza Oil Bleaching Through Optimized Acid Activation of Bentonite: A comparative study". Applied Clay Science, 42:336-344.
- Dubin, M.M (1960). "The Potential Theory of Adsorption of Gases and Vapour for Adsorbents with Energetically Non-uniform Surface", Chem. Rev.60:235-266.
- Egbuna, S.O, Ugadu, E, Ujam, A (2014). "Effects of Thermal Activation on The Physicochemical Properties of Natural White Clay as a Local Adsorbent". International Journal of Engineering Science Invention. 3:37-48.
- Ejikeme E.M., Egbuna S.O and Ejikeme P.C.N (2013), "Optimal bleaching performance of activated Ngwulangwu clay, International Journal of Engineering and Innovative Technology, 3(5):13-19.
- European Bentonite Association (EUBA), (2011), Bentonite, Industrial Minerals Association-Europe
- Farihausnah H., Mohamed K.A., and Wan Mohd Ashri Wan Daud (2011). "Textural characteristics, surface chemistry and activation of bleaching earth": A review, Chemical Engineering Journal, 170:90-106.
- Foletto, E.L., Colazzo, G.C., Volzone, C. and Porto, L. M (2011), "Sunflower oil bleaching by adsorption onto acid-activated bentonite". Brazilian Journal of Chemical Engineering, 28(01):169 - 174
- Foo, K.Y, Hameed, B.H (2010). "Insight into the modeling of adsorption Isotherm systems". Review Chemical Engineering Journal, 156:2-10.
- Gunay, A., Arslankaya, E., Tosun, I (2007). "Lead removal from aqueous solution by natural and pretreated clinoptilolite adsorption equilibrium and kinetics". J. Hazard Mater.146:362-371
- Hassan, M.S., and Abdel-Khalek, N.A., (1998), "Beneficiation and application of an Egyptian Bentonite", Applied Clay Science, 13:99-115



- Hobson, J.P (1969). "Physical adsorption isotherms extending from ultra-high vacuum to vapour pressure". J. Phys.Chem. 73:2720-2727.
- Hoffmann G (1989). "The chemistry and technology of edible oils and fats and their high fat Products". Academic Press Inc. London 164-167
- Horsfall.M.J, Ayebaemi, I. S (2005). "Equilibrium Sorption of  $Al^{3+}$ ,  $Co^{2+}$  and  $Ag^+$  in Aqueous Solutions by Fluted Pumpkin" (Telfairia Occidentalis HOOK f) Waste biomass. Acta Chim. Slov. 52:174-181
- Jalani, B.S, Rajanaidu, N (2000). Lipid Technol; 12 5 -8
- Kheok S.C, Lim, E.E (1982). "Mechanism of palm oil bleaching by montmorillonite clay activated at various concentrations". J. Amer. Oil. Chem. Soc. 59:129-131
- Lin, J., Zhao, G (2016). Preparation and Characterization of High Surface Area Activated Carbon Fibers from Lignin. Polymers 8:369
- Lugolobi, F (2016). bleaching Edible Oils Using Clay from Kangole, Morfo District, North Eastern Uganda. J. Anal. Bioanal. Tech. 7:320
- Madya D. R, Noor Azian Morad, Madya Mustafa Kamal, ABD Aziz, Rehani Binti Mohd. Zin (2006)."Process design in degumming and bleaching of palm oil". Centre for Lipids Engineering and Applied Research University Technology. Malaysia.
- Makhoukhi B., Didi M.A., Villemin D., and Azzouz A., (2009), "Acid activation of Bentonite for use as a vegetable oil bleaching agent". Grasas y Aceites, 60(4):343-349.
- Nadezda, S., Mihovil, L., Jelena, L., Jelena, P., Miljana, M., Biljana, B., Radosavljevic-Mihajlovic (2011). "Characterization of bentonite clay from "Greda" deposit". Processing and Application of Ceramics, 5(2):97-101
- Pantzaris, T.P (1995). Pocket book of palm oil uses. Palm oil Research Institute of Malaysia. Kaula Lumpur. Malaysia 158.
- Pesquera, C, Gonzalez, F, Benito, J, Blanco, C, Mendioroz, S, Pajares, J (1992). "Passivation of a montmorillonite by the silica created in acid activation" .Journal of Material Chemistry. 2:907-911
- Proctor, A. Brooks D.D (2005). Adsorptive separation of oils. Bailey's Industrial oil and Fat products. John Wiley and Sons 6<sup>th</sup> Ed.
- Rohani, B.M.Z; Madia, N.A.M; Madya, M.K.A (2006). Process design in degumming and bleaching of Palm Oil. University Teknologi Malaysia
- Sabah, E., Celik, M.S (2005). "Sepiolite and effective bleaching adsorbent for the physical refining of degummed rapeseed oil". J. Am. Oil. Chem. Soc. 82: 911-916.
- Usman, M. A., Oribayo, O., and Adebayo, A. A (2013), "Bleaching of Palm Oil by Activated Local Bentonite and Kaolin Clay from Afashio, Edo-Nigeria", Chemical and Process Engineering Research, 10:1-12.