

**SORBENT CHARACTERISTICS AND OPTIMIZATION OF BLEACHING PARAMETERS FOR COTTONSEED OIL USING MODIFIED OYSTER SHELL POWDER****O. A. Jeje¹, A. E. Okoronkwo², and O.O Ajayi¹,**¹Department of Basic Sciences, Federal Polytechnic Auchi, P.M.B 13 Auchi.²Department of Chemistry, Federal University of Technology Akure, P.M.B 704, Akure, Nigeria.Corresponding Author's e-mail: jaminjeje@gmail.com**ABSTRACT**

The optimum parameters for the bleaching of cottonseed oil (CTSO) using H₂SO₄ modified oyster shell powder (OSP) were investigated. Elemental analysis of the shell powder was performed using Energy Dispersive Spectroscopy (EDS) and the results indicated partial destruction of aluminum octahedral sheets with subsequent dissolution of structural cations. Results of the effect of contact time studied showed optimal bleaching of OSP was achieved within 45 minutes. Adsorbent dosage variation from 1.0g to 3.0g positively influenced the bleaching efficiency. The result of temperature study showed that the bleaching efficiency increases with increase in temperature from 35°C to 55°C. The thermodynamic parameters evaluated showed positive value of ΔH (803.96kJ/mol) indicating that the adsorption is endothermic. The negative value of ΔS (-6.668kJ/mol) suggested that the adsorption process is not reversible while positive values of change in Gibb's free energy (ΔG) show that the reaction is non spontaneous. The positive value of activation energy also indicated the endothermic nature of the adsorption process and the value of sticking probability $S^* < 1$ indicate that the probability of colour pigments to stick on the surface of the adsorbents is very high.

Keywords: oyster shell powder, adsorption isotherm, cottonseed oil**INTRODUCTION**

Oils and fats provided by nature are not always ideal for their ultimate use, whether for food or nonfood purposes and for this reason scientists and technologists have devised procedures for changing the natural oils. Purification of oil could be for nutritional, physical, and economic purposes. In edible oil refining, either by physical or chemical process, the bleaching stage is a critical step. The major objective of bleaching is the removal of colour pigments and the decomposition of hydro-peroxides. This increases the shelf life and aesthetic value of the final products (Baranowsky *et al.*; 2001). Thus the refining of vegetable oils through adsorptive bleaching remains inevitable in the oil refining industry (Bockisch, 1997).

Bleaching is an adsorption process that makes use of clay as adsorbent. Neutral clays, activated

earths, synthetic silicates and carbon black are the basic kinds of materials used in edible oil bleaching (Wiedermann 1981). Bleaching earth is composed of finely crystalline silicate of aluminium with various amounts of alkali metals and transition metals (Tsai *et al.* 2002). The bleaching clays are mainly aluminium silicates which are usually montmorillonite clays that exhibit adsorptive properties in both natural and activated states (Oboh *et al.*, 1987). Activated bleaching earths give higher activity when compare to crude clays. The major reason behind the use of bleaching clays is the elimination of various contaminants that can be divided into three groups. The primary contaminants are oil soluble compounds; proteins, sterols, tocopherols, hydrocarbons, and natural pigments. The secondary contaminants include; free fatty acids (FFAs), peroxides, ketones, aldehydes and the tertiary contaminants are; solvents, biocides, soaps, heavy metals (Fe³⁺

and Cu^{2+}), phosphoric and citric acid (Valenzuela et al. 2001). In order to ameliorate the adsorption properties and range of applicability, a number of physical and chemical methods have been investigated to modify the clays which include heat treatment, acid activation, treating the cationic surfactants and polymer modification (Chaisena and Rangsriwatananon, 2004; Al-Asheh et al., 2003; Motlagh et al., 2008; James et al., 2008). The use of activated clays in the bleaching of vegetable oils have been reported in the literature and prove successful (Christidis et al., 1997; Komadel et al., 1990; Rozic et al., 2010; Kirali and Lacin, 2006; Srasra et al., 1989) but few studies have been reported on the use of non- clay materials such as periwinkle shell powder (PSP), snail shell powder (SSP), oyster shell powder (OSP) etc, in the bleaching of vegetable oils. Therefore, the aim of this work was to modify Oyster Shell Powder by acid treatment and to evaluate its bleaching efficiency on cottonseed oil.

Materials and Methods

Cottonseed oil (CTSO) was bought from Gusau market in Zamfara State Nigeria while oyster shells were purchased from Warri, Delta state, Nigeria. The H_2SO_4 was of analytical reagent grade was used as obtained.

Adsorbent Characterization

The mineralogical composition of the raw and activated samples were determined using energy dispersive spectroscopy (EDS) while the structural morphology was investigated using Scanning Electron Microscopy.

Oyster Shell Powder Activation

Oyster Shell Powder (OSP) was prepared by washing with hot water to remove surface dirt, sun dried, ground and sieved using a 100microns sieve. The particles were activated by treating 250g of OSP with 100ml of $5\text{MH}_2\text{SO}_4$. The mixture was heated in a water bath at 80°C for 30minutes after which the solid phase was washed severally with distilled water in order to remove the residual acid, filtered, and dried in an electric oven at 105°C for two hours. The dried sample was ground and sieved again to the required particle size, and stored in a clean dry container until used.

Degumming

The oil was initially heated up to 60°C in order to melt before treatment with a food grade phosphoric acid of about 0.1% of oil weight with the acid concentration approximately 85%. It was stirred thoroughly for about 10 – 15 minutes. The aim was to decompose the non-hydratable phosphatides present in the oil as well as to coagulate the phosphatides making them insoluble and thus easily adsorbed during bleaching.

Bleaching of Cotton Seed Oil

The bleaching experiments were performed by batch method on a thermostatically controlled hot plate with stirrer and contact thermometer. Approximately 50g of degummed cotton seed oil was treated with 1.0g of activated adsorbent at 90°C for 30minutes. Afterwards the hot mixture was then filtered using whatman No. 1 filter paper.

Percentage Bleaching Efficiency

The bleaching efficiency of the adsorbent was determined by measuring the absorbance of bleached oil using a UV-Vis spectrophotometer at wavelength of 390nm. 2.5g of the filtered oil was transferred into 25ml standard flask and made up to the mark with n-hexane (w/v). The percentage bleaching efficiency of the oyster shell powder was determined as:

$$\text{Bleaching Efficiency \%} = \frac{A_o - A_t}{A_o} \times 100 \quad \dots (1)$$

Where; A_o and A_t are the absorbance of the unbleached and bleached oil samples.

Results and Discussion

Mineralogical Composition and morphological characteristics of the Oyster Shell powder

Elemental analysis results on table 1 provide evidence of the changes in the samples composition following modification. Regina and Okechukwu (2012) reported that acid activation of clay usually caused some modifications in the structure of the clays. During acid activation, interlayer cations are replaced with H^+ ions followed by partial destruction of aluminum octahedral sheets with subsequent dissolution of structural cations. The

increase in the surface area of the activated sample is as a result of elimination of the exchangeable cations, de-lamination of clay, which leads to the increase in micro-porosity during the activation process (Dias et al., 2003). The decrease in the octahedral sheet oxides;

Al_2O_3 , MgO , Fe_2O_3 along with the decrease in silica content proved that the original structure was altered. The result showed also the presence of sulphur in the matrix of H_2SO_4 treated sample.

Table: 1 Chemical composition of unmodified and modified OSP

% Elements Oxide content	Unmodified OSP	Modified OSP
MgO	0.802	0.60
Al_2O_3	2.87	1.13
SiO_2	0.77	0.11
CaO	77.9	39.20
Na_2O	0.7	ND
Fe_2O_3	13.8	9.8
S	ND	9.21
C	12.96	8.23
O	24.66	47.9
N	ND	ND

ND: Not Detected

The SEM micrographs of the adsorbent material showed that modification made the adsorbent material looked more porous than

the unmodified. Figure 1b showed the oyster shell powder in a plate-like shape after being modified using H_2SO_4 .

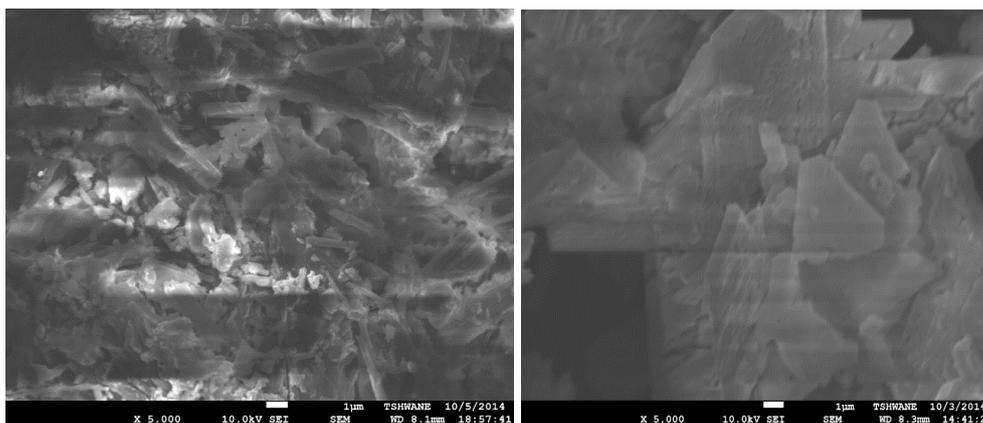


Figure 1. SEM micrographs of (a) untreated and (b) H_2SO_4 modified OSP

Effect of contact time on bleaching efficiency

Figure 3 shows the effect of adsorbate resident time on bleaching efficiency by OSP. It is observed from the curve that the bleaching efficiency increased with contact time up to an optimum time of 45 minutes. The increase in colour pigment removal by OSP in the first 15 to 45 minutes can be due to the increased availability of vacant sorption sites at the initial stages. The optimal contact time of 45 minutes is

in accordance with the work of Berbesi (2006), who reported that the contact time for effective bleaching normally ranges from 15 to 45 minutes. It is also observed that at the attainment of adsorption equilibrium at 45 minutes, the bleaching efficiency of OSP decreases, this could be as a result of adsorption equilibrium tending towards desorption and some of the adsorbed pigments dissolve back into the oil (Dubrakva et al. 2012).

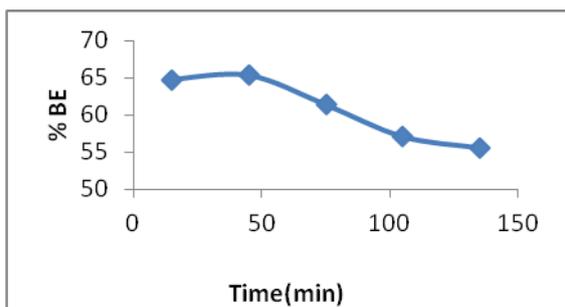


Figure 2: Effect of contact time on bleaching efficiency at 90°C

Effect of dosage on bleaching efficiency

Figure 3 shows that the bleaching efficiency increased with increasing OSP dosage. This suggests that the active sorption sites available increases as the dosage increases for the colour pigments adsorption. Therefore, it may be concluded that impurities such as Fe₂O₃, CaO and MgO that cover part of the active sites are removed by acid activation and the number of active sites available for adsorption increased (Salawudeen et al., 2007).

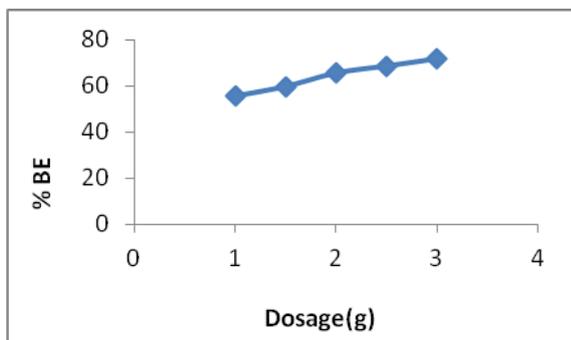


Figure 3: Effect of Dosage on Bleaching Efficiency at 90°C

Effect of Bleaching Temperature.

The percentage bleaching efficiency increases with increase in temperature as evident in figure 4. This might be due to the fact that chemical reactions take place on the surface of the adsorbent and leads to increase in kinetic energy of the reaction of both desirable and undesirable materials in the oil from 2 to 4 folds with a temperature increase of about 10°C (Brdicka 1965). The bleaching efficiency increased with temperature to a maximum at 55°C and then tends towards equilibrium thereafter.

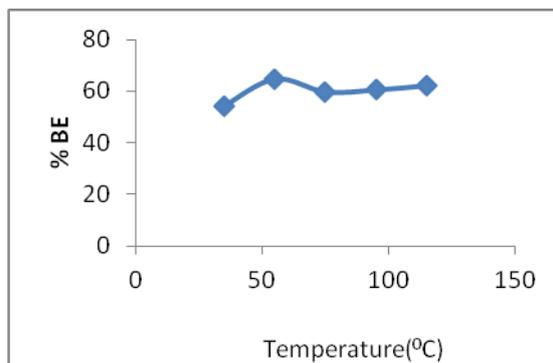


Figure 4: Effect of Temperature on Bleaching Efficiency

Adsorption isotherms

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 of equation 2 below:

$$\frac{X_e}{x/m} = \frac{1}{ab} + \frac{1}{a}X_e \dots\dots\dots 2$$

Where x = amount of solute adsorbed, X_e = amount of unadsorbed solute, m = grams of adsorbent used, ‘a’ is the surface area of the adsorbent (m²/100g), and b is a constant of the intensity of the adsorption.

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

$$\frac{x}{m} = kc^n \dots\dots\dots 3$$

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 (Jimoh et al., 2011). 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).

$$\log \frac{x}{m} = \log k + n \log c \dots\dots\dots 4$$

This study revealed that increase in temperature enhances the rate of pigment adsorption as also reported by Ajembaa *et al.* (2012). This is an indication of increase in kinetic energy of the colour pigments which increases the frequency of collisions between the adsorbent and colour pigments and then increases the adsorption of pigments on the surface of the adsorbent. The adsorption isotherm models' constants and the correlation coefficients (R^2) are reported in Table 2. The correlation coefficient values for all the adsorbents are 0.7734 for Langmuir and 0.959 for Freundlich. The values obtained for Freundlich model suggests that it is the best isotherm model to describe the adsorption process (Fig. 4 & 5). A similar conclusion was reported by Nwabanne and Ekwu (2013) and also conforms to the report of Rohani (2006) that Freundlich isotherm is more applicable to a liquid phase.

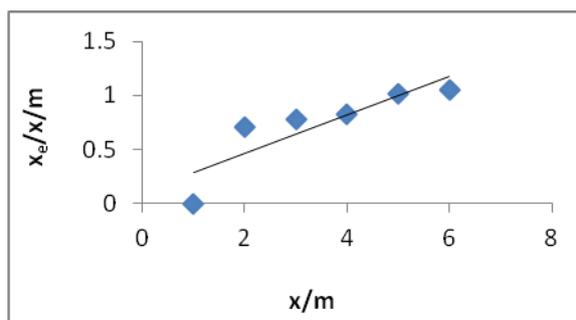


Figure 4: Langmuir isotherm model for the bleaching of CTSO

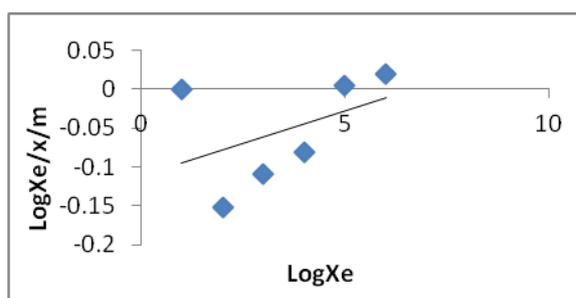


Figure 5: Freundlich isotherm model for the bleaching of CTSO

Table 2: Langmuir and Freundlich isotherm parameters for the bleaching of cottonseed oil with OSP modified with 5M H₂SO₄

Langmuir Isotherm			Freundlich Isotherm		
Q_{max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2
0.641	-1.377	0.773	3.076	1.847	0.959

Kinetic studies

The applicability of the Pseudo-first-order and Pseudo-second-order models was tested for the adsorption process. The best fit model was selected based on the R^2 values (Figures 6 and 7). The Pseudo-first- order equation is given as:

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \dots\dots\dots 4$$

Where q_e and q_t refers to the amount of dye adsorbed (mg/g) at equilibrium and at any time

t (min) respectively, and K_1 is the equilibrium rate constant of Pseudo-first-order adsorption.

The integration of equation 3 with the initial condition, $q_t = 0$ at $t = 0$ (Lagergren 1898), gives;

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \dots\dots\dots 5$$

The slope and intercept of plot of $\log (q_e - q_t)$ against t were used to determine the Pseudo-first-order rate constant K_1 for the adsorption process.

The HO's Pseudo-second-order kinetic model used to interpret the experimental data is presented as;

$$\frac{t}{q_t} = \frac{1}{K^2 q_e^2} + \frac{1}{q_e} t \dots\dots\dots 6$$

The slope and intercept of plot of t/qt against t were used to calculate the second-order-rate constant K₂.

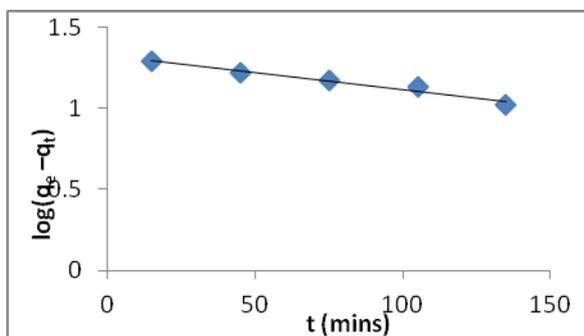


Figure 6: Pseudo-first order kinetic model for the bleaching of CTSO

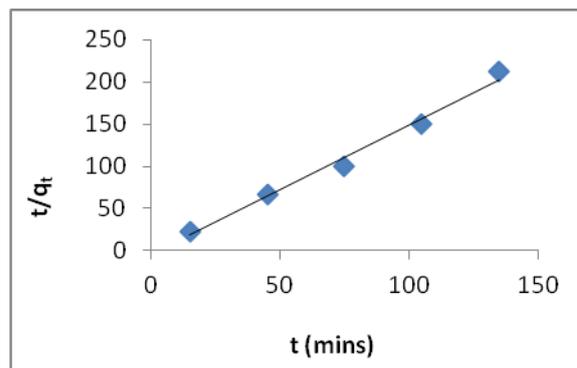


Figure 7: Pseudo-second order kinetic model for the bleaching of CTSO

Linear plots of the kinetic equations and the values of the parameters are reported in Table 3. From the R² values which range between 0.969 (Pseudo-first order) and 0.998 (Pseudo-second order), it can then be inferred that the adsorption process is best described by Pseudo-second order model.

Table 3: Pseudo-first- order and Pseudo-second- order kinetic model parameters for the bleaching of CTSO with OSP modified with 5MH₂SO₄

Pseudo- first-order model			Pseudo- second-order model		
K ₁ (1/min)	q _e (mg/g)	R ²	K ₂ (g/mg min)	q _e (mg/g)	R ²
-49.06	10.26	0.969	-0.508	0.65	0.988

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 ΔG, change in enthalpy ΔH and change in entropy ΔS. The Van't Hoff equation used to determine the value of the equilibrium constant with temperature changes is given as:

$$\Delta G^o = -RT \ln K \dots\dots\dots 7$$

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R} \left(\frac{1}{T}\right) \dots\dots\dots 8$$

The values of ΔH and ΔS were obtained from the slope and intercept of the graph by plotting lnK against 1/T. The equation for change in free energy is;

$$\Delta G^o = \Delta H^o - T\Delta S^o \dots\dots\dots 9$$

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 (θ). The S* is a function of the adsorbate/adsorbent system and it is the measure of the ability of an adsorbate to remain on the adsorbent indefinitely. It is expressed as:

$$S^* = (1 - \theta) \exp\left(-\frac{E_a}{RT}\right) \dots\dots\dots 10$$

$$\text{Log}(1 - \theta) = \text{log}S^* + \frac{E_a}{RT} \dots\dots\dots 11$$

Where; θ is surface coverage, E_a is activation energy.

$$\theta = \left(1 - \frac{C_e}{C_0}\right) \dots\dots\dots 12$$

Where C₀ and C_e are the initial and equilibrium concentration respectively. The values of E_a and

S^* were obtained from the slope and intercept of the graph by plotting $\log(1-\Theta)$ against $\frac{1}{T}$.

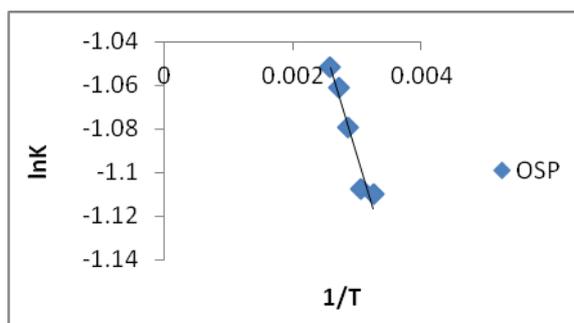


Figure 8: Plot of LnK against $1/T$ for the adsorption of CTSO onto OSP modified with 5M H_2SO_4

Table 4: Thermodynamic parameter for the bleaching of CTSO

Temp.(K)	ΔG (kJ/mol)	ΔH (J/mol)	ΔS (kJ/mol)	E_a	S^*
303	2824.36	803.96	-6.668	0.0665	0.5568
328	2991.01				
348	3124.42				
368	3257.78				
388	3391.14				

The values of thermodynamic parameters are reported in Table 4. The values of change in Gibb's free energy (ΔG) obtained are all positive in the adsorption process. The values show that the reaction is not spontaneous and this suggests that the adsorption reaction will not proceed at ordinary laboratory working temperature. The positive values obtained for the change in enthalpy (ΔH) of the adsorption process indicate that the adsorption process of colour pigments in CTSO is endothermic in nature. It was observed also that the value of change in entropy (ΔS) of the adsorption process in OSP modified with H_2SO_4 is negative. The observed negative value suggested that the adsorption process is not reversible. The positive values of activation energy (E_a) indicate the adsorption process is endothermic in line with the change in enthalpy of the adsorption process. The sticking probability (S^*) values indicate that the probability of colour pigments to stick on the surface of the adsorbents is very high since $S^* < 1$. Horsefall and Spiff (2005) had reported similar observation in adsorption process.

Conclusion

The study shows that modified OSP follows the adsorption isotherm models tested but the best fit isotherm is Freundlich isotherm model having

the higher R^2 value. The Pseudo-second order kinetic model better interpreted the experimental data. The thermodynamics parameters also revealed the endothermic nature of the adsorption process and the non-spontaneity of the process. Therefore, modified OSP is a viable adsorbent for the bleaching of cotton seed oil.

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