COMPARATIVE ADSORPTION STUDY OF OYSTER SHELL, PERIWINKLE SHELL AND KAOLIN IN THE BLEACHING OF PALM OIL

By

A. E. OKORONKWO
Department of Chemistry,
Federal University of Technology,
Akure.

And

AYORINDE O. JEJE
Department of Basic Sciences,
Auchi Polytechnic,
Auchi.

Abstract

This work has been initiated to assess the feasibility of bleaching of palm oil using activated marine shells(oyster and periwinkle shells) and kaolin. The oyster shell(OS), periwinkle shell (PS), and kaolin (K) were activated using different concentrations of H_2S0_4(1M, 3M, 5M). The effect shows that bleaching efficiency increases as the concentration increases but more better in kaolin. The study revealed that these materials are good adsorbents that can be used for palm oil bleaching. Their adsorption conforms with the models of Freundlich and Langmuir isotherms. The use of these materials is therefore recommended for the bleaching of palm oil.

Refining process is a necessary step for the production of edible oils and fats products, either by physical or chemical process, the degumming and bleaching treatments are critical steps in edible oils and fats refining. The objective of this process is to remove unwanted impurities and other components, which will affect the quality of finished products. Leong(1992).

For bleaching process, bleaching clays are used. Neutral clays, activated earths, synthetic silicates, and carbon black are the basic kinds of materials used in edible oil bleaching(Wiedermann 1981).The principal goal of the use of bleaching clays in the elimination of a series of contaminants which comprise for example phosphatides, free fatty acids, pigments(such as carotene, chlorophyll), odours and flavours (including aliphatic aldehyde and ketone), waxes as well as trace metals.(Valenzuela 2001).The removal of pigment and other various trace constituents by adsorption process is one of the most important steps in the vegetable oil refinery.

Palm oil is used mainly for cooking such as cooking oil, margarine and shortening but also has non-food applications such as soap, detergent; cosmetics etc.

Pristine

Clay features are strongly dependent on the activation procedure. The acid treatment is expected to improve the specific surface area, porosity, pore volume and size and also make the surface acidic. While the bleaching power of clay is very high, efforts have been made to promote the efficiency of other locally sourced materials such as OS, PS, and K by varying acid concentration. Studies carried out so far on the previous research work shows that much has not been carried out on the application of OS, PS in bleaching of vegetable oils. Therefore, the main objective of this study is to investigate, and evaluate the suitability and applicability of the shells powder in vegetable oils bleaching.

Materials and Methods

Both shells(oyster and periwinkle) were obtained from Warri in Delta State while Kaolin was obtained from Okpella (Edo State). The crude palm oil was obtained locally from Warrake market. Sulphuric acid used is of analytical grade. The chemical composition of the shells and kaolin were given in Table 1

Preparation of Samples

The OS and PS were washed with hot water, and then rinsed with distilled water and sun dried for several hours. The sun dried shells and kaolin were crushed, ground to powder form. The oyster shell (OS), periwinkle shell (PS) and kaolin (K) were sieve using 250 micron mesh size which were used in activation process.

Acid Activation

The samples were treated with H_2SO_4 solution at chosen concentrations of 1M, 3M, 5M and acid/clay ratio of 0.4. 100ml of H_2SO_4 was added to 250g sample suspended in water. The mixture was maintained at a temperature of 100^OC for 30 minutes. The resulting mixture was filtered washed with hot distilled water and dried in an electric oven at 105^0C.

Bleaching Process

The bleaching process was carried out by adding 100g of degummed oil and 2g of activated samples into a Pyrex glass(250ml) and heated at constant temperature of 90^oC on a hot thermostatically controlled electric plate with stirrer for 30 minutes. The mixture was filtered to separate the bleached oil from the bleaching sample.

Analysis of Bleaching Performance

The absorbance of unbleached(crude) palm oil and bleached palm oil was measured using a UV-VIS Spectrophotometer. Bleaching efficiency was evaluated by monitoring the absorbance at 450nm as given by the following formula.

$X = A_o - A_t/A_o$ where X is the relative amount of pigment adsorbed, A_o is the absorbance of unbleached oil, A_t, is the absorbance of bleached oil at time t.

$X_e = A_t/A_o = 1-X$ where X_e is the residual relative amount at equilibrium.

Table 1. % Chemical Composition of the Sample

	SIO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	K_2O	MgO
Oyster shell	44.4	9.2	0.08	0.59	45.0	0.05	0.44
Periwinkle shell	44.0	7.4	1.5	1.7	47.0	0.29	0.34
Kaolin	78	4.8	4.3	0.42	10.8	0.65	1.0

Results and Discussions

The absorbance of unbleached (crude) palm oil is 3.390 at 450nm and the values of absorbance are given in table 2, at different acid concentrations. The bleaching efficiency increases as the concentration increases, since the absorbance decreases as the acid concentration increase; it shows that the relative amount of pigment adsorbed increases while the residual relative amount at equilibrium decreases for the bleaching of palm oil.

Table 2. The value of absorbance at 450nm each adsorbent at different acid concentrations

	Absorbance		
Conc (M)	OSP	PSP	K
1	0.358	0.360	0.352
2	0.277	0.276	0.262
5	0.263	0.268	0.245

Table 3. The value of % adsorbed by

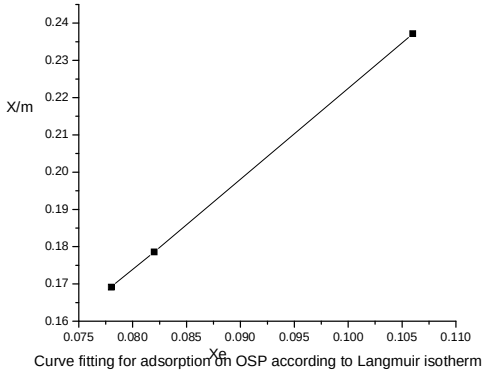
	Percentage Adsorbed		
conc(M)	OSP	PSP	K
1	89.4	89.3	89.6
3	91.8	91.9	92.3
5	92.2	92.0	92.8

Table 3 shows the percentage colour reduction of palm oil obtained by the activated shells and clay samples at different concentration of sulphuric acid. They all show increase in adsorption activity as the concentration of sulphuric acid increases but it is more in kaolin

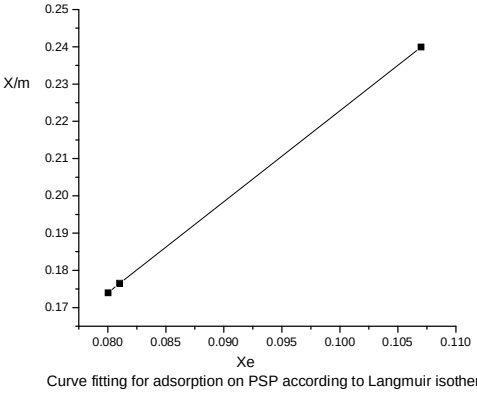
The effectiveness of the shells was further investigated using the concept of isotherm models(Langmuir and Freudlich). The assumption of Langmuir adsorption isotherm relates the amount of adsorbate per unit mass of adsorbent to the residual relative amount at equilibrium for bleaching process according to equation 1Achife,(1989). Langmuir equation also assumes that the surface is homogenous. Way, S ,Boyjoo, Y, Chouib.(2005)

$(X_e)/x/m = 1/a + (b/a)X_e$. (1) Where ais the surface area of the solid. From the equation (1)aplot of $(X_e)/x/m$ against X_e should give a straight line with slope equal to b/a and the intercept equal 1/a. Figure Ia -IIIa shows Langmuir plot for the bleaching of palm oil**.**

Pristine

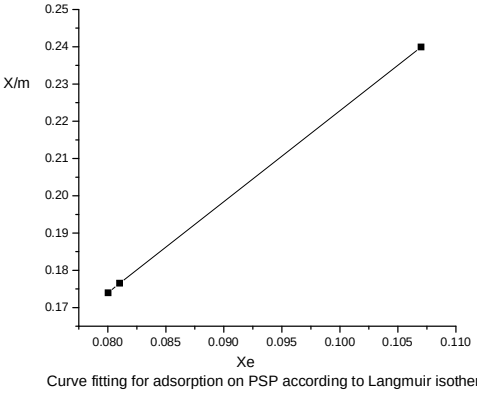


Curve fitting for adsorption on OSP according to Langmuir isotherm



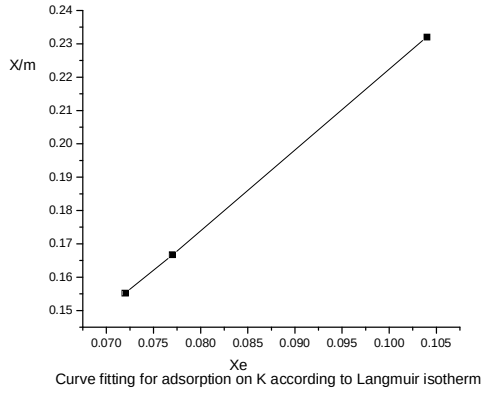
Curve fitting for adsorption on PSP according to Langmuir isotherm

Fig Ia



Curve fitting for adsorption on PSP according to Langmuir isotherm

Fig IIa



Curve fitting for adsorption on K according to Langmuir isotherm

FigIIIa

The values of Langmuir constants are recorded in table 4. From the result, it was found that the surface areas of oyster, periwinkle, and kaolin are 0.4116, 0.4095, and 0.4150 respectively. This indicates that their surface areas are similar while that of kaolin is slightly higher. This shows while the adsorption efficiency of kaolin is slightly higher.

Table 4 Shows Langmuir Constants

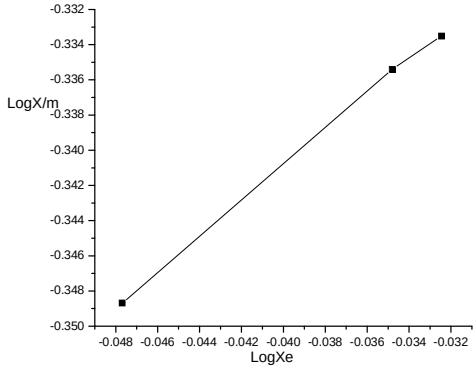
	b	a	R^2	Surface area
OSP	2.4294	-2.044x10-2	0.99997	0.4116
PSP	2.4417	-2.136x10-2	0.99999	0.4095
K	2.4051	-1.853x10-2	0.99991	0.4150

A series of complex intractions controls the adsorption process during vegetable oil refining. Proctol, A,Toro-Vazqes,J.E. (1996).The Freundlich adsorption isotherm was originally developed to explain the adsorption of a single solute from solution. However, a similar adsorption pattern had been observed when studying a complex system of adsorption of vegetable oil pigments on bleaching earths. Thus, the Freundlich has been useful in evaluating the commercial value of adsorbents

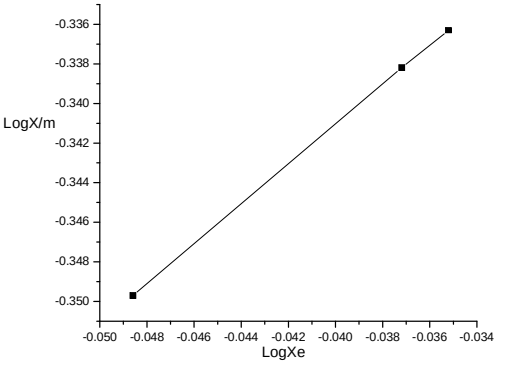
Base on Freundlich adsorption isotherm, the fraction of surface coverage (x/m) is related to the residual relative amount at equilibrium according to equation(2) Achife, (1989).$X/m = KX_e^n$.Freudlich equation is valid for any method of colour measurement, as the units of measurement are additives and proportional to the actual concentration of colouring materials in the oil (Hui, 1996).

Taking logarithm on both sides of equation(2). $Log(x/m) = logK + nlogX_e$;where K and n are Freundlichconstants.figure 1b-111b.show Freundlich plot for the bleaching of palm oil

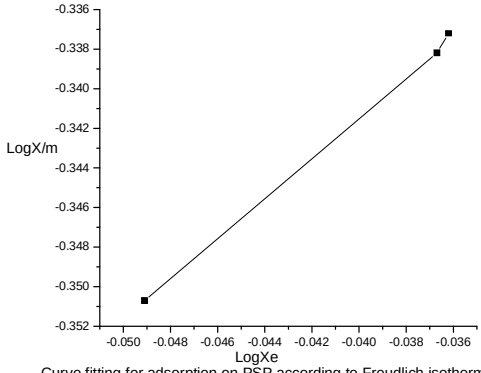
Pristine



Curve fitting for adsorption on K according to Freudlich isotherm
Fig Ib



Curve fitting for adsorption on OSP according to Freudlich isotherm
Fig IIb



Curve fitting for adsorption on PSP according to Freudlich isotherm
Fig IIIb

For the adsorption by OS, PS, K. values of Freundlich constant n and k are recorded in table 5

Table 5. **Showsfreundlich Constants**

	n	k	R^2
OS	1.0089	0.5221	0.99835
PS	1.0288	0.52260.99791	
Kaolin	1.0030	0.52150.99989	

The data were fitted in straight lines using the technique of regression analysis. The value of k determines the degree of decolourisation within which the adsorbent exhibit its greatest relative effect, and n is an indication of its characteristic manner of adsorption (Noris, 1982). The values of k obtained for the three adsorbent indicates that they are efficient in the bleaching of palm oil. Also the values of n lies between 0 and 1 indicating favourable adsorption and large surface for adsorption.(Rayakorn 2008).

Conclusion

Acid treatment of oyster and periwinkle shells and kaolin gave rise to an effective bleaching and base on their relative values of adsorption capacity, available surface area, % sorption, they show a high level of good adsorbents that can be used in the bleaching of palm oil.

Recommendation

As a result of the performance of acid activated oyster and periwinkle shell powder as well as kaolin, the adsorbents are recommended for the bleaching of vegetable oils since they are readily available and inexpensive.

References

Achife, E.C., Ibemesi, J. A. (*1989)*.Suitability of bentonite for the bleaching of cotton seed oil.*J. Am. Oil Chem.Soc.* 66, 247

Hui, Y. H. (*1996*).*BaIley's Industrial Oil and Fat Products*.5thEdn.New York.John Willey and sons Inc

Leong, W. L. *(1992*). *The Refining and Fractionation of Palm Oil Mill Engineers-Executives.* Training Course with semester. PORIM. Bangi.1-6.

Noris, F. A. *(1982*).*Bailey's Industrial Oil and Fats Products*, 4thEdn. Edited by D. Swern, A Wiley-Interscience Publication, John Wiley and Sons,New York, NY,pp.294-314.

Okeke, J. A. (*1990*).*Reforming of Sheanut Oil,* MSc. Thesis.UNILAG.

Proctor, A. & Toro-Vazques, J. E. (*1996*) The Freundlich Isotherm Studying Adsorption in Oil Processing, *JAOCS*, 78, 1627-1633.

Rayakorn, N. (*2008*). *Elimination of Phorbol Esters in Seed oil and press Cake of JatrophaCurcas L.*Master of Science Thesis. Kasetsart University. 22

Valenzuela Diaz, F, Souza Santos, P, (*2001*). Studies on the acid activation of BrazillanSmectitic clays. *Quim Nova* 24.343-353.

Way, S., Boyjoo, Y, Chouib. (*2005*). *Chemosphore*, 60(10).1401-1407.

Wiedermann, L. H. (*1981*). Degumming, Refining, and Bleaching Soybean Oil. *JAOCS*.159-165