Original research Article

POTENTIAL APPLICATION OF OYSTER SHELL AS ADSORBENT IN VEGETABLE OIL REFINING

ABSTRACT

Aim: Generation of filter materials from the shell of invertebrates for the removal of hazardous components from fluid is receiving low attention, both in industry and in academia. However, the shell of invertebrate like oyster has a very high potential in removing color pigments and other impurities in water and vegetable oils. In order to utilize the adsorption potential and to control the disposal effects of oyster shell on the environment, this work studied its effectiveness as adsorbent in vegetable oil refining.

Methodology: Activated and un-activated oyster shells were produced and each was separately used as adsorbent in the bleaching process of Palm Kernel Oil (PKO). The micro-structural images of the adsorbents produced were studied using SEM. The physicochemical properties of PKO before and after the bleaching process were monitored and compared. The performance evaluation of the adsorbents was further substantiated by using Freudlich and Langmuir adsorptions isotherms

Results: SEM images showed a clear difference on visual observation with higher degree of porosity in carbonated oyster shell. The physicochemical properties after adsorption bleaching showed that the carbonated oyster shell has more adsorptive power in its pure and natural form than when chemically activated with H_2SO_4. A maximum of 96.97 and 94.44 percentage color reductions for un-activated and activated oyster shells were achieved respectively. K and n values obtained from the isotherms (constants for a given adsorbate and adsorbent at a particular temperature) were 0.397 & 0.567 and 12.373 & -0.459 respectively for un-activated and activated adsorbents. Reduction were also observed in the percentage free fatty acid and iodine value after the adsorption process with both adsorbents but more reduction were noted in the PKO refined with un-activated oyster shell.

Conclusion: Oyster shell can be effectively used as adsorbent in vegetable oil refining. These results confirmed the effectiveness of the oyster shell in color and particulate removal.

Key Words: Adsorption Isotherms, Oyster Shell, Palm Kernel Oil, Vegetable Oil

1. INTRODUCTION

Oyster shell contributes adversely to the environmental management in the coastal regions, especially places where fishery appears to be a highly profitable business and oyster as dominant products of shellfish farm. Such industry has a potential of serious problems about disposal of oyster shell waste and hence constitute a nuisance to the environment. Gil-Lim [1] analyzed the chemical composition of oyster shell indicated that more than 90% of the shell is $CaCO_3$ (95.99%) while others are clay minerals like SiO_2,(0.69%) Al_2O_3 (0.42%), MgO, (0.65%) P_2O_5, (0.20%) Na_2O, (0.98%) SrO (0.33%) and SO_3 (0.72%) present in minute quantities. The presence of clay minerals, particularly SiO_2 and Al_2O_3, contributes to the high adsorptive property of oyster shell [2].

Vegetable oil is widely used as edible oil and industrially as base stock in the production of lubricants and grease, as well as candles, paints and resins. In most industrial applications most especially oleochemical industries, Refined, Bleached and Deodorized (RBD) oil are used. Hence, remover of pigments, and other various trace constituents of the oil is one of the major steps in the vegetable oil refinery and it is best perform by adsorption process.

Adsorption is a separation process in which a solute in a liquid is deposited at surface of a solid termed the adsorbent [3], [4]. It could be physical or chemical depending mainly on the interaction between the solute and the solid. At ordinary temperature, physical adsorption predominates and results from intermolecular forces while at elevated temperatures, chemical bond are either broken or created due to the increase in activation energy and form the bases for chemical adsorption commonly referred to chemisorptions [5], [6], [7]. Adsorption is indicative in most natural physical, biological, and chemical systems, and is widely used in industrial applications [8].

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). Various isotherms developed includes Langmuir, Freudlich, Multisite, Lattice gas and Bet Isotherms [9].

The mechanisms for the adsorption in oil bleaching industry are different and diverse [2]. Noorlida [10] in his work found that the removal of carotene from palm oil/hexane miscella by activated rice hull was due to chemisorptions. Proctor [11] concluded that adsorption of luxein from soy/hexane miscella on rice hull ash was a physical adsorption process while that on activated clay was a chemical adsorption.

Adsorbent is an important filter material for the removal of hazardous components in exhaust gases or liquid, for the purification of drinking water, waste water treatment, or for refining purposes in vegetable oil industries. It can be in form of activated carbon, carbon nano-tubes, silica gel or activated clay [12], [13], [14]. Because of their wide range of use, the demand on adsorbent is high and will rise in future.

Little attention has been given to economic value of shells of invertebrates like oyster shell, rather they are disposed off and consequently become nuisance in the environment. This work studied the effectiveness of activated and unactivated oyster shell as adsorbent in vegetable oil refining. This will reduce the amount of solid waste in the environment and consequently produce raw materials for industrial use.

2. MATERIALS AND METHOD

2.1 Materials

Oyster shell was obtained from Kuatan, Malaysia while the palm kernel oil was obtained from Nigeria Institute for Palm Oil Research, Benin Nigeria. The reagents used include sodium hydroxide, sodium thiosulphate solution, starch solution, glacial acetic acid (2 %), potassium iodide, ethanol, phenolphthalene (indicator) and hydrochloric acid (0.5 M). All the reagents are of analytical grade. The major equipment used are: Electric furnace, electric oven, water bath, Atomic Absorption Spectrophotometer, Field Emission Scanning Electron Microscope, Colorimeter, pH meter and mercury thermometer.

2.2 Methods

2.2.1 Preparation of adsorbent from oyster shell

The oyster shell was washed thoroughly with water in a beaker and then dried in an oven maintained at 60 ºC for 24 h. This was followed by crushing with mortar and pestle. 200 g of the crushed oyster shell was made into slurry by soaking in 0.1 M H_2SO_4. The resulting mixture was heated at 100 ºC to dryness as acid activated oyster shell. Dried acid treated oyster shell was calcined at a temperature of 400 ºC in an environmentally controlled furnace for 1-hour and allowed to cool. The calcined activated oyster shell was washed in a filtration set to remove the residual acid using distilled water. The residue was dried, pulverized and sieved as the activated adsorbent produced from oyster shell. UN activated adsorbent was made by calcinating the raw oyster shell and then pulverized and sieved.

2.2.2 Scanning Electron Microscope

The surface morphology of the raw and modified oyster shell samples were evaluated using Field Emission Scanning Electron Microscope (JOEL JSM-5600). The oyster shell powder was sprinkled on the sample holder and then coated with a thin gold layer prior to examination using sputter coater. The samples were then mounted on the scanning microscope to view their structural images.

2.2.3 Degumming of Crude Palm-kernel Oil (CPKO)

250 ml of crude palm kernel oil was measured into a 1 liter beaker and followed by addition of boiled distilled water (300 ml). The mixture was mixed vigorously in the beaker (1liter capacity). The entire mixture was poured in a separating funnel to remove the gums. The process was carried out three times to ensure complete removal of all the hydratable gums [15].

2.2.4 Neutralization of palm kernel oil

Neutralization of PKO was carried out by addition of 8.0 ml of 0.5 M NaOH solution into 100ml of degummed oil. The mixture was mixed thoroughly in a beaker. 2 g of common salt was added to facilitate the separation of neutral oil and the soap formed. The neutral oil was filtered from the mixture using vacuum filtration set.

2.2.5 Bleaching of Palm Kernel Oil

35 g of the degummed and neutralized PKO was measured into a beaker of 250 ml capacity. This was followed by addition of the activated oyster shell (10% weight of oil) into the oil. The mixture was heated in a water bath at 120 ºC with continuous stirring for 20 minutes. After the adsorption period, the mixture was filtered and the bleached oil collected. The percentage color reduction was calculated by using the Equation 1. This same procedure was adopted when un-activated adsorbent was used. The collected oil was then subjected to various analyses.

2.2.6 Determination of Percentage Colour Reduction (%CR)

The percentage colour reduction of the oil after bleaching was determined using colorimeter (Uniscope, SM-3004). A full absorption spectrum was made between 420 nm and 670 nm. The result showed that maximum absorption occurred at 530 nm. The absorbance of the samples was determined at the maximum absorbance wavelength (530 nm). The samples were diluted in n-hexane in the proportion 0.1g of oil to 2 ml of solvent [16]. The bleaching capacity of the adsorbent was determined using the following relation:

$$\%CR = \frac{Ab_O - Ab_x}{Ab_O} * 100 \qquad (1)$$

Where Ab_O and Ab_x represents absorbance of the crude palm kernel oil and bleached palm kernel oil respectively.

2.2.7 Determination of Free fatty Acid (FFA)

Acid value and free fatty acid content of the oil before and after bleaching was determined using titrimetric method [17]. Oil sample (2.5g) was accurately weighed in a 250 ml conical flask and 50 ml of ethanol and 1ml of phenolphthalein was added to it. The mixture was boiled for 2 minutes and titrated while still hot against standard potassium hydroxide solution (0.1M) in a 25 ml burette under rigorous shaking until the persistence of the pink colour for about 15 seconds. The acid value was calculated from the amount of titrant used using the following relation.

$$Acid\ value = \frac{V \times N \times 56.11}{M} \qquad (2)$$

Where, V is the volume of Potassium hydroxide used in ml, N is the exact molarity and M is the mass in g of oil sample.

The free fatty acid was inferred from the acid value according to equation 2

$$\%\ \text{Free fatty acid (FFA)} = 0.503\ \times\ \text{acid value} \qquad (3)$$

2.2.8 Determination of Iodine value

The iodine value of the oil was determined using titrimetric method [18]. Oil sample (0.1 g) was weighed into a 300 ml stoppered flask and 20ml of carbon tetra chloride was added. The oil was allowed to dissolve. Iodine bromide (25ml) was also added and the stopper was inserted again. The mixture was gently shaken and kept in the dark for 1hr. Potassium Iodide (20 ml) and 150ml of water was added to the mixture. The mixture was then titrated against standard sodium thiosulfate (0.1 M) until the yellow color due to iodine as almost disappeared. A few drops of starch was then added as indicator and the titration was continued with rigorous shaking until the blue colour just disappeared. The iodine value was calculated from the following relation:

$$iodine\ value = \frac{(b-a) * 0.01269 * 100}{weight\ \ (in\ g) of\ substance} \qquad (4)$$

Where, a is the number of ml of sodium thiosulphate, b is the volume of titrant in ml.

2.2.9 Effectiveness of adsorbents produced using adsorption isotherms

The adsorptive bleaching was carried out using the standard procedure. The mass of adsorbent was varied between 1 to 3% of PKO (w/w). The results were subjected to Freudlich and Langmuir adsorption Equations given in Equations 5 and 6:

$$Log\ q_e = nlogC_e + logk \qquad (5)$$

$$\frac{C_e}{q_e} = \frac{1}{q_e K_L} + \frac{1}{q_m} C \qquad (6)$$

Where, q_e, q_m, K_L and C_e, are the amount of solute adsorbed on the adsorbent at equilibrium, maximum adsorption capacity, constant related to the free energy of adsorption and equilibrium concentration of the solute in the bulk solution.

3. RESULTS AND DUSCUSSION

3.1 Microstructure Analysis of the Oyster Shell Sample

Figure 1 (a), (b) and (c) show the micro-structural images of the raw oyster shell, calcined or un-activated oyster shell and acid activated oyster shell. It is clearly shown in Figure 1 (a) that the oyster shell in its pure natural form exhibited a coarse micro-structural image. Comparing Figure 1 (a) with (b) and (c), it was observed that the image is less coarse after calcination and became finer after acid treatment. This is an indication that the treatment had effect on the microstructure and possibly more surface area which will definitely enhance adsorption of pigment to the surface of the adsorbent. However, adsorption experiment shows that the calcined oyster shell was more effective than the acid activated oyster shell. This may be attributed to the effect of acid attack on some active site on the surface of the material. Washing of the activated oyster shell after acid treatment may also be a contributory factor for the decreased efficiency.

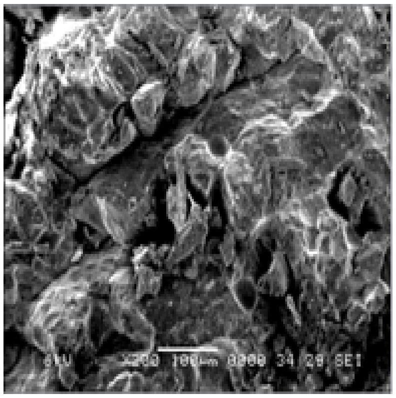

Figure 1 (a): Raw Oyster Shell

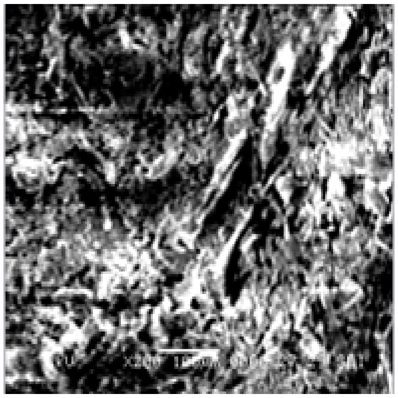

Figure 1 (b): Calcined Oyster Shell

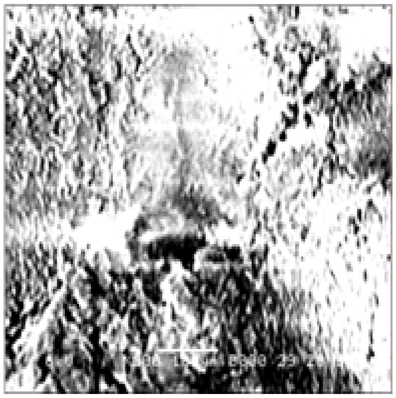

Figure 1 (c): Acid activated Oyster Shell (1000×)

3.2 Color and Percentage Color Reduction

Figure 2 shows the graph of mass of adsorbent used relative to the absorbance and percentage color reduction in the PKO.

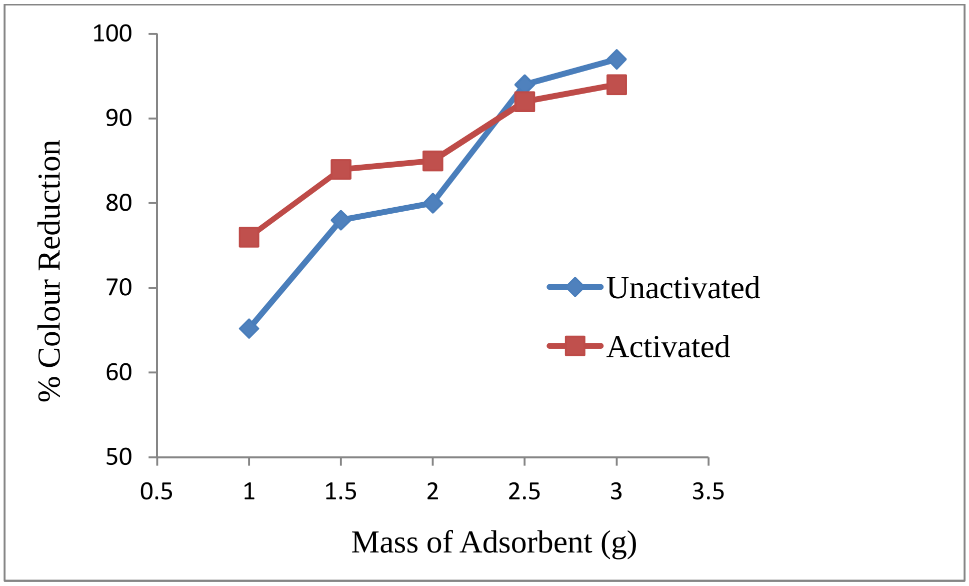

Figure 2: Percentage colour reduction (%CR) of activated and unactivated adsorbent

The graph shows that the efficiency of both un-activated and activated oyster shell measured in terms of percentage color removal is higher at 3 g (10% mass of the PKO) and this corresponds to the maximum of 96.97% CR and 94.44% respectively at the same quantity of adsorbent. Point “A” in the figure, where the two plots intersect signifies a point where either of the adsorbents gives equal %CR. This implies that above 2.5g (8.33% mass of PKO), un-activated oyster shell has a better adsorption capacity than acid activated one and should therefore recommend for such process for economic reason.

3.3 Physicochemical Properties

Table 1 shows the physicochemical properties of crude PKO and refined PKO using 3g of the adsorbent. Generally, the values of these properties after neutralization with NaOH were 7.74, 3.32% and 16.50 for acid value, percentage free fatty acid and iodine value respectively. It is clearly indicated that most of the properties decreases after treatment with adsorbent.

Table 1: Physicochemical Properties of PKO Before and After Refining

	Oil Properties			
Material/Adsorbent	Acid value (mg/kg)	% FFA	IV (mg/kg)	Colour
Crude Oil	7.74	3.88	16.6	Light brown
PKO + COS	6.72	3.37	16.5	Light brown
PKO + UOS	4.4	2.21	13.69	Light yellow
PKO + AOS	6.4	3.22	16.49	Light yellow

COS = Crude Oyster Shell
UOS = Unactivated Oyster Shell
AOS = Activated Oyster Shell
IV = Iodine value
FFA = Free fatty acid

3.4 Acid value (AV)

The acid value (AV) is the number of milligrams of alkali required to neutralize 2 g of fat or oil. It determines the level of saturation or unsaturation depending on the type of fatty acid present in the PKO. From the table, an appreciable reduction in the AV is observed when both un-activated and activated oyster oil was used in the refining process but un-activated oyster shell is more effective when compared with activated sample with 4.40 and 6.40 mol/Kg AV respectively. This is an indication that apart from color removal, un-activated oyster shell performs better in terms of acid reduction when compared with acid treated sample. This could be traced to the residual acid used for activation that could be added to the free fatty acid in the PKO.

3.5 Iodine value (IV)

A higher IV usually indicates problems with fractionation process and the yield of palm kernel stearing. The result as indicated in the Table 1 above shows a sharp reduction (from 16.50 to 13.69) in the IV when un-activated oyster shell was used but no significant effect was observed when activated shell was employed in the process. This therefore justified the claim that carbonized and unactivated oyster shell has a better adsorptive power than acid treated one.

3.6 Isotherms Studies

Freundlich equation is useful in color measurement as long as the units of measurement are additives and proportional to the actual concentration of coloring materials in the oil [2], [3]. Table 2 shows compared the Freundlich adsorption constant (n and k) for both the activated and un-activated oyster shells. The adsorption constants were estimated by plotting ln C_e versus ln q_e. The n and k values as determined from the slope and the intercept of the graph respectively for un-activated was 0.3158 and 0.461while for activated was 12.824 and -0.4881. High n-value (12.824) in activated oyster shell indicated that the un-activated shell proved to be more effective than activated one. This is because n-value determines the degree of decolorization within which the adsorbent exhibit its greatest relative effect. If “n” is high, the adsorbent is relatively inefficient as an agent for effecting high degree of decolorization, but for low n-value (<< 1), reverse is the case [19] [20]. The linear coefficient (R^2) shows the fit between the experimental and calculated values of the models. However, k value is just a general measure of the activity of the adsorbent, the negative value obtained for the activated oyster shell is also an indication that unactivated oyster shell is more efficient [8].

The Langmuir isotherm model was also used to fit the adsorption of pigment on the adsorbent. The linearized model (Type 1) was used to estimate the model parameters, q_m and K. The Langmuir parameter were estimated by plotting the C_e/q_e versus C_e. The calculated parameters from the plots are shown in Table 2. The maximum adsorption capacity q_m (0.14488) for the unactivated oyster shell is higher than the q_m (-0.08356) activated oyster shell. This shows the effectiveness of the unactivated oyster shell over the activated oyster shell.

It is obvious from the two isotherm models fitted that the unactivated oyster shell is more effective than the activated oyster shell. However, the best fitted model was chosen to be Langmuir model because of its higher correlation coefficient (0.9749) compared to Freundlich isotherm model (0.9343).

Table 2: Isotherm parameters

	Langmuir Isotherm			Freundlich isotherm		
Parameters	q_m	K_l	R^2	n	K	R^2
UOS	1.4488	9.804	0.9749	0.3158	0.461	0.9343
AOS	-0.08356	-0.8882	0.9762	12.824	-0.4881	0.9902

Conclusion

Adsorbents have been developed from oyster shell using acid activation and carbonization in the presence of Nitrogen as a purging gas. SEM images showed a clear distinction in three samples on visual observation. The effectiveness of the adsorbents produced was tested on PKO and the un-activated oyster shell has better adsorption capacity compared to acid treated oyster shell and crude oyster shell. This result was substantiated by using Freundlich and Langmuir adsorption isotherms which gave better adsorption constant in favor of un-activated oyster shell. The best isotherm model that fits the adsorption experiment is Langmuir isotherm model. Base on these facts, it is therefore concluded that oyster shell (solid waste) can be effectively used as a raw material for the production of adsorbent.

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