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Optimal Adsorptive Bleaching of Palm Oil with Activated Beans Husks

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Abstract

The effectiveness of activated bean husks for the adsorptive bleaching of palm oil was studied in this work. Optimal bleaching parameters like temperature, time and adsorbent-oil ratio were determined for the palm oil decolouration. Various weights of 1, 1.5 and 2 g of activated beans husks were contacted with crude palm oil at 50, 80, 110, 140 and 170 °C and contact times of 45, 60 and 90 minutes using 20 ml of oil sample in each case. The decolorizing effect increased linearly with temperature. Optimal adsorption conditions gave a bleaching efficiency of 98%. Langmuir, Freundlich, Temkin with Dubinin-Radushkevich isotherms were correlated, and Freundlich has the highest statistical correlation coefficient (R^2) value of 0.9901. Dubinin-Radushkevich isotherm suggested chemisorption. The pseudo-second-order model provided the best fit for the kinetic study.

Keywords: Beans husks, adsorption, isotherms and kinetics, optimization, palm oil bleaching

Introduction

Bleaching crude palm oil is a well-researched area of food engineering and development. However, probing into previous efforts revealed bleaching earth, kaolin, clay, bentonite and clay-derived substances mainly as adsorbents in this field. Comparative analysis has also been presented. Some previous accounts are given in the literature [1-15].

The activation of bentonite was conducted by impregnating bentonite particles with saponin solution at various mass ratios as reported by Kalidikalam *et al.* [16]. Their bleaching process reported that the saponin-modified bentonite could adsorb about 310 mg of carotenoid per g of the adsorbent. Nnanwube *et al.* [17] also reported some degrees of achievements with Ogbunike Kaolinite. They presented optimum bleaching conditions of 2.62 hours, 106.83 ºC, 3.32 g clay dosage and 0.17 mm particle size. They further reported that 73.35 % of pigments were removed using Response Surface Methodology. Kaolinite from Ibusa as an effective adsorbent also removed pigments from palm oil by Okafor *et al.*, [18]. Their bleaching process investigated the variation of clay dosage plus acid concentration for treatment and temperature also. Their highest removal of pigments was about 97.4% in 80 minutes. Their data were best suited by the Temkin isotherm and pseudo-second-order kinetic models. Nando clay's usefulness in palm oil's bleaching had been reported by Nwabanne *et al.* [19]. Their acid-activated clay results suggested a rise in temperature and adsorbent dosage raised the bleaching efficiency, while an increase in particle size reduced it.

Adsorbents derived from other sources apart from these materials like agro-wastes are fewer in the literature. Crude palm bleaching with activated plantain peel ash (APPA) was reported by Raji *et al.* [20]. The optimization and correlation of temperature, time and adsorbent dosage to the percent bleaching efficiency were done in their work. They reported the highest adsorption efficiency of 70.04% at 160˚C, 60 minutes and adsorbent dosage of 4 g. In another development, oil palm boiler ashes (OPBA) produced from a boiler in mills was used in refining palm oil as an alternate bleaching adsorbent by Lau *et al.* [21]. The effectiveness of OPBA in their raw, enhanced and pelletized forms was studied for bleaching efficiencies on carotenoid removal at various operating conditions. Their final refined oil colour of 4.0R was obtained using 0.05 wt% of enhanced OPBA at 110 °C for 45 min under constant agitation (300 revolutions per minutes) and subsequent deodorization at 265 °C for 1 h. The study indicated enhanced OPBA as substitutes to commercial bleaching earth for producing comparable refined oil colour rating, which could reduce production cost. Other alternative adsorbents reported in the literature have a varying degree of achievements [22-28].

The production of inexpensive adsorbents remained a significant challenge in the commercial production of refined palm oil. Better production techniques with inexpensive raw materials are being studied, especially agro-wastes as an alternative with low inorganic and high carbon contents. Several bio-sorbents have been used to produce activated carbon, such as *macadamia* nut-shell, apricot stones, coconut shells, sugarcane bagasse, corn cobs, plantain peels, sawdust, rice husks, and sago wastes, to mention a few [20]. As far as we know, beans husks have remained unexplored for their bleaching potentials for palm oil bleaching.

This work, therefore, presents the optimum adsorptive bleaching of palm oil with beans husks. This was achieved through characterization and activation of the beans' husks, evaluation of the bleaching efficiency compared with relevant previous works, and studies on the effect of contact time, temperature, and adsorbent weight on the bleaching of palm oil as identified process parameters.

Materials and Methods

To ensure data reproducibility, all recorded experimental values are averages of three runs.

Materials and Equipment

These include beans husks collected from Agege market in Lagos State, Nigeria, analytical grade potassium hydroxide, hydrochloric acid, orthophosphoric acid, isopropyl alcohol, sodium hydroxide, acetic acid, chloroform, potassium iodide, sodium thiosulphate, isooctane chemical, measuring cylinders, weighing balance 2010 (SSP 01 BL model), mortar and pestle, crucible, beakers, conical flasks, flat-bottom flasks, electric oven (Bockel DZF-6020 model), muffle furnace (model LF 3), Whitman No. 1 filter paper, stirrer, burette, magnetic stirrer hot plate (model number BST/MS 51), retort stands, 300 mm mesh, stop watch, United Kingdom

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(UK) ultra violet (UV) spectrophotometer (Jenway UV 2600 model), distilled water, pH meter (Jenway 3510 model), German Lovibond tintometer (model Gardco F).

Production of Activated Carbon

Steps taken involved pre-treatment of the beans husks sample in which seeds were separated from the husks, husks washed with deionized water, sun-drying to remove water and oven drying at 120 °C. This was followed by carbonization of the beans' husks in which samples of the precursor after pre-treatment were heated to 500 ºC in the muffle furnace for 1 hr and then allowed to cool. The carbonized husks were crushed and sieved with a mechanical sieve to obtain desired particle sizes. This was followed by chemical activation with orthophosphoric acid used as the activating agent for an impregnation ratio of 2:1. This formed a slurry by vigorously mixing the activating agent with some carbonized husks in a container. A 1 N H_3PO_4 solution was prepared for the chemical activation. The slurry was oven-dried for 24 hours at 120 °C and allowed to cool. After cooling, the sample was heated in the furnace at 700 °C for 30 minutes. Figs. 1, 2 and 3 show the pre-treated, carbonized and activated beans husks, respectively. The final step was acid washing by soaking the activated carbon in 0.1 N HCl for 24 hours and washing with distilled water until the pH was 6 - 7.

Figure 1: Pre-heated Beans Husks at 120 ºC.

Characterization of Produced Activated Carbon Adsorbent

Moisture Content

The method adopted followed Otaru *et al.* [29]. A petri-dish was oven-dried after washing. Two grams of the sample were then weighed into a petri dish. The weight of the sample and petri dish was recorded before drying in the oven. The petri dish and sample were kept in the oven for 30 minutes at 120 °C and the resulting weight was recorded. The drying operation was repeated until a constant weight was obtained (± 0.01 g). The % moisture content was calculated with Eq. (1).

$$\% \text{ moisture content} = (W_1 - W_2)/W_3 \quad (1)$$

w_1 and w_2 are weights of the petri dish containing the original and dried samples, respectively, while w_3 is the weight of the original sample used.

Figure 2: Carbonized Beans Husks at 500 ºC

Figure 3: Activated Beans Husks at 700 ºC

Ash Content

This was determined by following the method of Otaru *et al.* [29]. Five grams of the activated carbon sample was dried at 80 °C for 24 hours and placed in the weighed furnace container. The sample was heated in the muffle furnace at 650 °C for 3 hours. The sample was then cooled to ambient temperature before weighing. The percent ash was calculated with Eq. (2).

$$\text{Ash } (\%) = (WS_3 - WS_2)/WS_1 \quad (2)$$

WS_3 (g) is the weight of the furnace container containing heated ash, WS_2 (g) is the weight of the furnace container and WS_1 (g) is the weight of the original activated beans husks used.

Yield (%)

This was determined by adopting the method of Otaru *et al.* [29]. The activated carbon yield, which is a ratio of the product's final weight after washing and drying to the initial material's weight, was evaluated with Eq. (3).

$$\text{Yield } (\%) = W_f - W_o / W_0 \times 100 \quad (3)$$

W_f and W_o are the weights of the final activated carbon and dried carbon before activation, respectively.

Bulk Density

The experimental procedure of Oyetola and Abdullahi [30] was adopted. A measuring cylinder was used to measure out 20 ml of water. Another measuring cylinder was used to measure weighed beans husks ash poured into the water inside the first measuring cylinder. As the volume of the water increased, the volume of water initially in the cylinder (V_1) was subtracted from the new volume of the water (V_2). The volume change was divided by the bean's husks ash's weight to calculate the bulk density.

Pore Volume

The experimental procedure by Smith [31] was adopted. The adsorbent's total pore volume was determined by boiling an already weighed sample of the adsorbent immersed in water. After the air in the samples was displaced, the samples were carefully dried and weighed. The pore volume was obtained by dividing the weight increase by the density of water.

Iodine Number (IN)

By adopting Ekpete *et al.* [32] method, the sample was placed in a 250 cm^3 conical flask and 10 cm^3 of 5% HCl was added to it and stirred. Later, a 100 ml iodine solution made by dissolving 2.7 g of iodine and 4.1 g of potassium iodide in one liter of deionized water was standardized with a solution of 0.1 M sodium thiosulphate. The iodine solution was then added to it while shaking the mixture for 20 mins. The mixture was later filtered with filter paper. A 30 ml aliquot portion was then titrated with 0.1 M sodium thiosulphate using a starch indicator. The percent iodine adsorbed by each activated carbon was calculated with Eq. (4).

$$IN = ((Na_2S_2O_3 volume\ in\ blank - Na_2S_2O_3 volume\ in\ sample) / Na_2S_2O_3 volume\ in\ blank) \times 100 \quad (4)$$

Determination of the pH

Ekpete *et al.* [32] method was followed. Activated carbon weighing 2 g in 50 ml of distilled water was stirred for 30 mins. The filtrate was tested for pH using a pH meter.

Batch Bleaching of Palm Oil

The method of Usman *et al.* [33] was adopted. The crude palm oil absorbance was determined first with a UV spectrophotometer to serve as the control value. Various temperatures (50, 80, 110, 140, and 170 ºC), various weights (1, 1.5 and 2 g) and various times (45, 60 and 90 mins) were carefully selected to vary one parameter per run. Twenty milliliters of crude palm oil was poured into a beaker, followed by heating to 50 ºC on a magnetic hot plate. One gram of the activated sample representing an adsorbent-oil ratio of 5% was added to the heated oil while maintaining the temperature at 50 ºC. The mixture was afterward filtered with a Whatman No. 1 filter paper. This procedure was repeated with activated samples of 1.5 and 2 g representing adsorbent-oil ratios of 7.5 and 10% respectively at 50 ºC and 45 mins. The procedure was also repeated for the effect of temperature at 80, 110, 140 and 170 °C as well as 60 and 90 mins selectively per run.

Evaluation of the Bleaching Performance

By following the method of Usman *et al.* [33] with the completion of each bleaching, the beaker content was filtered with a Whatman No.1 filter paper and the pigment concentration in the filtrate was determined. The evaluation of the pigment amount was done by UV spectroscopy. The samples were diluted in acetone to a concentration of 10 % (v/v), and the absorbance of each sample was determined using the UV spectrophotometer. The bleaching performance of the adsorbent was determined with Eq. (5).

$$\%\ Bleaching\ \text{Performance} = (ABS_0 - ABS_1)/ABS_0 \quad (5)$$

ABS_0 and ABS_1 are the absorbances of crude and bleached palm oil, respectively.

Free Fatty Acid (FFA) of Bleached Palm Oil

The method of Ismail *et al.* [34] was adopted. Fifteen bleached palm oil samples and a sample of the crude palm oil were placed into separate conical flasks and marked accordingly. These samples were then heated until they become melted on a magnetic hot plate surface to ease mixing. To each of the oil samples was added exactly 30 ml of isopropyl alcohol (IPA). Titration was done with sodium hydroxide of 0.1019 N while swirling the solution until the oil mixture samples, IPA and sodium hydroxide turned light red. The amount of sodium hydroxide used per oil sample was noted and the FFA calculated by Eq. (6).

$$\text{FFA Value} = (25.6 \times \text{Titre Value } (TV_f) \times N_c) / (\text{Mass of bleached palm oil}) \quad (6)$$

TV_f is the quantity of sodium hydroxide titrated and N_c is the molar concentration of sodium hydroxide.

Peroxide Value (PV) of Bleached Palm Oil

The method of Ismail *et al.* [34] was followed in this study. An acetic acid-chloroform mixture in ratio 3:1 was mixed into a conical flask with the bleached palm oil. All oil samples weighed 4 g. Another sample was also crude palm oil that has not yet undergone any bleaching process. A 5 ml potassium iodide solution was added into each of the oil mixtures and left in a dark place for a minute before proceeding to the next step. About 2 ml of starch was added into the solution, which caused a reaction to occur and made the color of the solution turned black. Titration was carried out in conical flasks with each mixture that has turned black until the solution turned colorless. The sodium thiosulphate amount used in the titration was noted. The calculation of the peroxide value is given by Eq. (7).

$$PV = TV_p \times N_t / \text{Mass of bleached palm oil} \quad (7)$$

TV_p is the volume of sodium thiosulphate titrated, while N_t is the molar concentration of sodium thiosulphate fixed at 10.25 N.

Carotene Value of Bleached Palm Oil

Following Ismail *et al*. [34] method, all oil samples were heated until they become melted on a magnetic hot plate surface to ease mixing. The heated oil samples were poured into flat bottom flasks and weighed on a weighing balance with various weights ranging from 0.25 to 0.27 grams. All 15 oil samples in the flat bottom flasks were then mixed with isooctane until the solution's level reached the level marked on the flat bottom flasks. Each oil sample was then placed into the UV spectrophotometer. The carotene value for each sample was determined and recorded.

Colour Analysis of Bleached Palm Oil

According to Hunt and Pointer [35], the 15 bleached and one crude palm oil sample were placed in conical flasks. The samples were poured into a rectangular fused glass cell (dimension 2.54 cm by 13.36 cm). The glass cells were placed inside Lovibond Tintometer equipment. The samples were arranged in two adjacent fields of view, which were visible through the viewing tube. They were placed in a way that the product in the sample field and another white reflective surface in the comparison field were comparable sides by the sides.

Results and Discussion

Adsorbent Development and Characterization

As seen from Table 1, the carbonization of the beans' husks with activation resulted in higher adsorption potentials than carbonization without activation. The fact is that the activated bean husk sample resulted in increased total pore volume, % ash content, decreased bulk density and decreased % yield of the adsorbent. The increase in total pore volume could be caused by the destruction of the aliphatic and aromatic species initially present in the raw materials leading to quick removal of volatile matters during the activation process. These volatile matters are by-products of organic materials and minerals present in the activated carbon surface. The reduction of the volatile matter in the activated carbon caused a high percentage of non-volatile ash. The increase in the pore volume caused less carbon to occupy more space, which led to a decrease in bulk density. Due to the reduced % yield with increased carbonization temperature, production losses become imperative in choosing the carbonization temperature for activated carbon production. Iodine adsorption is a quick and straightforward technique to ascertain the adsorptive capacity of activated carbon. The iodine value for activated carbon using phosphoric acid activation at 700 °C indicated an increase in impregnation ratio and increased iodine value. The increase in iodine value resulted from the formation of pores in the carbon. The high iodine value was due to the husks of the beans - acid ratio of 2:1. The Physico-chemical properties are within the ASTM D2866-11 standards specification [36].

Fourier Transform Infrared (FTIR) Analysis

The plotted spectra of the raw and acid-activated beans' husks are presented in Figs. 4 and 5, respectively. In Fig. 4, the coupled vibrations are significant due to the various constituents. A peak exists at 3140.25 and 2479.87 cm^{-1}, indicating –OH functional group. The –OH group belongs to water molecules. On the left side, there are peaks at 1403.21, 976.84, 872.15, and 551.90 cm^{-1}. These correspond to the aromatics, C=C, C-F, =C-H, arene, and C-Br functional groups. The absence of these bands in the chemically activated carbon spectra indicated that the phosphoric acid acted as a dehydrating agent, thus increasing aromatization.

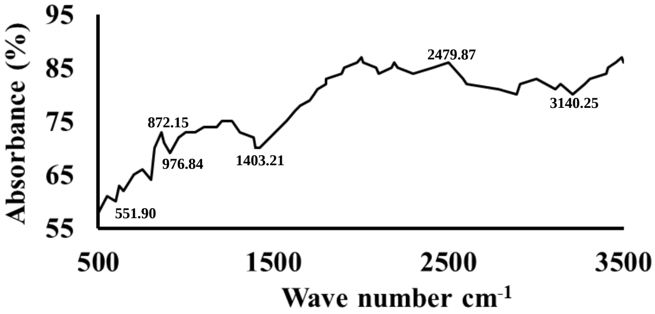


Figure 4: FTIR Spectra of Carbonized Beans Husk.

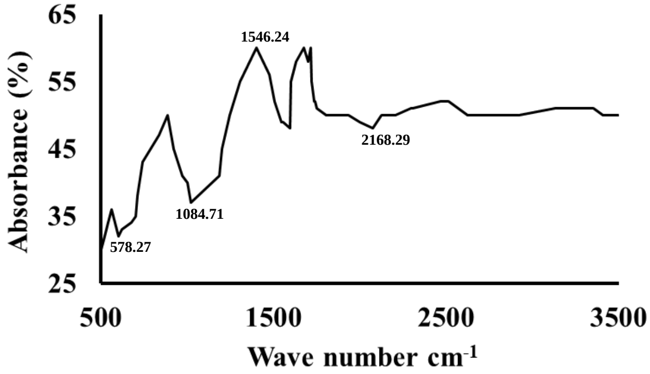


Figure 5:. FTIR Spectra of Activated Beans Husk.

The chart also shows high absorbance values for the functional groups; the lowest absorbance value is about 60 %. In Fig. 5, there are no frequency peaks on the right part of the chart. On the left, there are peaks at 578.27, 1084.71, 1546.24 and 2168.29 cm^{-1}. These correspond to the C-C triple bond, alkyl group, C=O carboxylic acid group, and NO nitro group. The last peak at 578.27 cm^{-1} corresponds to the C-C triple bond. These functional groups contributed to the adsorption of sulphur compounds onto the activated carbon. The efficacy of the chemically activated carbon is strongly related to their surface organic group. Also, the chart shows low values of absorbance, with the largest value around 60 %.

Physico-chemical Properties of Crude Palm oil

The Physico-chemical properties of the crude palm oil used are given in Table 2. The low value of the FFA shows that the palm oil used was fresh. As palm oil ages, its FFA increases owing to hydrolysis in the presence of water and heat. The iodine value depicts that palm oil is a non-drying oil and the higher the iodine value, the higher the level of unsaturated fatty acids present. Palm oil, therefore, finds use in applications where oxidation is undesirable. Also, the high saponification value suggested that palm oil is helpful for soap production.

Free Fatty Acid (FFA) Value

The FFA content appears to be the most used criterion for accessing palm oil quality because it must have moderate values. The presence of free fatty acids in palm oil points to impairment in the oil quality. From the result displayed in Table 3, the bleached oil using sample 4b obtained under conditions of 140 °C, 60 minutes and 1.5 g of adsorbent required the smallest quantity of sodium hydroxide for titration.

Table 2. Physico-Chemical Properties of Crude Palm Oil

Parameter	Values
Density	0.8889 g/ml
Free Fatty Acid (FFA)	5.478 ml.mol/g
Peroxide Value	4.702 ml.mol/g
Carotene Value	2.549
Iodine Value	50 g/g
Saponification Value	202.42 mg KOH

Absorbance of Bleached Palm Oil

Table 3 shows the results of the activated beans husks bleaching of the crude palm oil sample. These were labeled 1a - 5c with the crude palm oil sample and the effectiveness on colour reduction expressed in ranges. Absorbance values were determined at 520 nm wavelength.

Peroxide Value (PV)

Peroxide value is an indication of oxidation or rancidity of palm oil. Excess exposure of palm oil to oxygen lowers the oil quality. Therefore, a high peroxide value should be avoided as it only brings adverse effects to the oil constituents. The dark color contained in palm oil is usually affected by oxidation. This is evident when the cooking oil turns black when it is repeatedly used for frying. Besides rancidity and dark color, high peroxide value is also connected with bad odor, as the oil becomes exposed to oxygen during frying. From Table 3, bleached sample 4a obtained at 140 °C, 45 mins and 1 g adsorbent, adsorbed the highest amount of peroxide, while sample 5c gave the highest peroxide values of 3.356 ml.mol/g. This was because the oil sample was heated to a high temperature of 170 °C. Peroxide value is susceptible to heat and excess temperature.

Carotene Value

The carotene content in the crude and bleached palm oil samples is given in Table 3. Carotene content in palm oil needs to be retained for good health benefits. The result in Table 3 revealed that sample 1a obtained under 50 °C, 45 mins, and 1 g with 2.474 was the best. The carotene value in bleached palm oil must be maintained at about 80 % of the crude sample. For samples 5a-5c, the carotene content contained in the oil was below 80 % and this was due to the excessive heating at 170 °C. Carotene content in palm oil is susceptible to heat and excess temperature.

Table 1. Effect of Activation on the Properties of Beans Husks

Parameter	H_3PO_4 Activated Beans Husk Carbon	Carbonized Raw Material	ASTM D2866-11 Range [36]
(%) Yield	59.4 %	64.8 %	-
(%) Moisture content	8.5 %	9.6 %	3 – 10 (max)
(%) Ash content	4.7 %	1.2 %	< 8 % (max)
Bulk Density (g/ml)	0.7	0.79	0.36 – 0.74
Pore Volume (cm^3/g)	2.05	1.45	2.0 - 3.5
pH	7.1	-	-
Iodine Number	1250.6 mg/g	322.69 mg/g	-
Particle size (µm)	50	90	30-110

Table 3. Results for Absorbance, FFA, Peroxide, Carotene and Colour Values

Sample Interpretation	Absor-bance	FFA Value ($ml.mol.g^{-1}$)	Peroxide Value ($ml.mol.g^{-1}$)	Carotene Value	Colour
1a: 50 °C, 45 mins, 1 g	0.800	4.630	2.306	2.474	45Y+14.6R
1b: 50 °C, 60 mins, 1.5 g	0.710	4.109	2.460	2.391	38Y+12R
1c: 50 °C, 90 mins, 2 g	0.650	3.714	2.537	2.277	26Y+11R
2a: 80 °C, 45 mins, 1 g	0.542	3.326	2.563	2.240	24Y+10R
2b: 80 °C, 60 mins, 1.5 g	0.489	2.740	3.049	2.186	22Y+10R
2c: 80 °C, 90 mins, 2 g	0.386	2.543	3.383	2.109	18Y+9R
3a: 110 °C, 45 mins, 1 g	0.302	2.348	2.255	2.007	17Y+8R
3b: 110 °C, 60 mins, 1.5 g	0.241	2.276	2.614	1.996	15Y+6R
3c: 110 °C, 90 mins, 2 g	0.136	2.250	3.459	1.981	14Y+6R
4a: 140 °C, 45 mins, 1 g	0.060	2.015	2.010	1.979	11Y+4R
4b: 140 °C, 60 mins, 1.5 g	0.070	1.989	2.434	1.970	12Y+5R
4c: 140 °C, 90 mins, 2 g	0.069	2.022	2.691	1.967	12Y+7R
5a: 170 °C, 45 mins, 1 g	0.076	2.230	3.075	1.465	10Y+8.5R
5b: 170 °C, 60 mins, 1.5 g	0.079	2.283	3.331	1.250	11.5Y+8R
5c: 170 °C, 90 mins, 2 g	0.081	2.315	3.536	1.147	11Y+5R
Crude Palm oil	2.045	5.218	4.613	2.602	58Y+17.9R

Colour

In Table 3, the colour change of the palm oil samples was recorded. The best reduction in color with sample 4a marked the lowest at 11Y + 4R, followed by sample 4b with 12Y + 5R. Y and R are Yellow and Red readings with coefficient values of 1 and 0.5, respectively. The Y signifies the degree of yellowness of the oil under daylight illumination, while the R signifies the rosins present in the form of a reddish-orange colour.

Effect of Contact Time

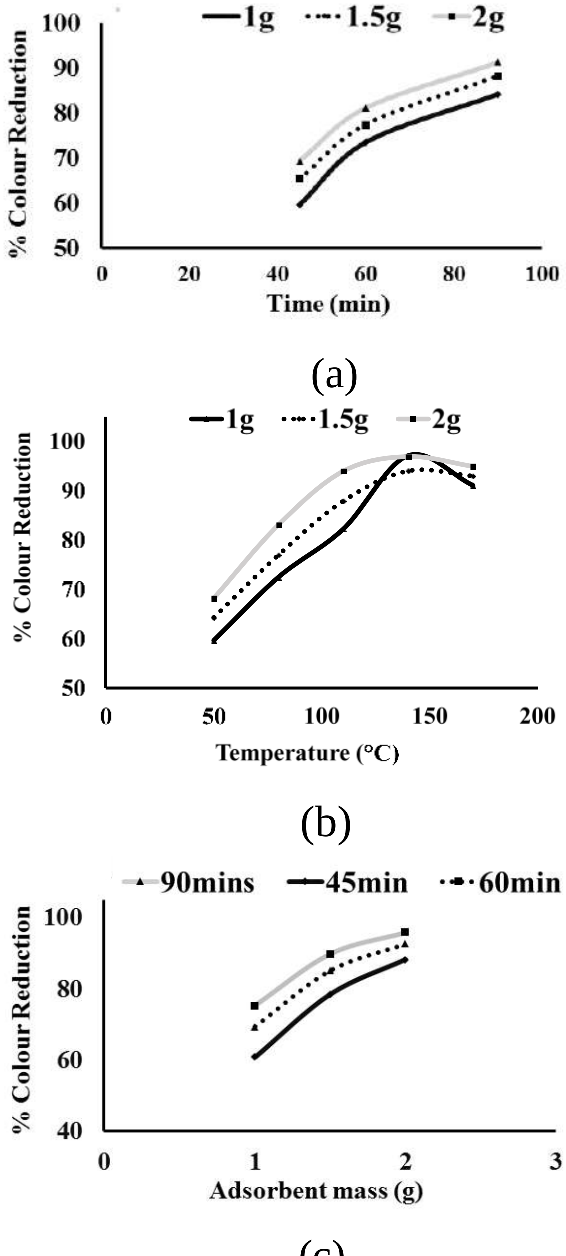
The effect of contact bleaching time for the acid-activated beans' husks at 50 ºC for 1, 1.5 and 2 g adsorbent are shown in Figure 6a. Different times ranging from 45 to 90 minutes were used. Adsorptive bleaching efficiency increased as time increases. The highest and best bleaching time was 90 minutes. Further improvement in % colour reduction (CR) of palm oil did not occur after this contact time. Therefore, determining optimum bleaching time is crucial as prolonged bleaching time may lead to colour deterioration with higher temperatures. Statistical evaluation with Analysis of Variance (ANOVA) and Bonferroni-Holm Posthoc test was computed with Daniel's XL Toolbox Version 6.70. The degrees of freedom between groups (D_{FB}) value was 3, the degrees of freedom within groups (D_{FW}) value was 8. The Fisher's ratio (F) value was 316.25, a desirable high commendable value signifying a good relationship among the variables. The probability factor (P) was 1.20×10^{-8}, which was less than the critical probability factor (P_C) with a value of 0.05 in the 95% confidence interval depicting good statistical relevance. The Bonferroni-Holm Posthoc significance test of the CR at various weights for time is shown in Table (4). The CR at all weights was significant with time.

Effect of Temperature

Figure 6b revealed that the bleaching efficiency was favored by temperature increase for 45 mins and 1, 1.5 and 2 g adsorbents as the temperature increased from 50 to 140 °C, and later decreased at 170 ºC. The bleaching efficiency increased due to access to adsorption sites below 170 ºC. Optimization is imperative to establish high bleaching efficiency without unwanted phenomena. The D_{FB} was 3, D_{FW} was 16, F value was 26.478, which is commendable, showing a good variable relationship. P value was 1.92×10^{-6}, which was smaller than the P_C value of 0.05 at the 95% confidence interval. The Bonferroni-Holm Posthoc significance test of CR at various weights for temperature is shown in Table (5). The CR for the various weights used were all significant with temperature.

Effect of Adsorbent Weight:

Fig. 6c shows the bleaching efficiency plot with adsorbent weight for 45, 60 and 90 mins at 50 ºC. Dosage increment increased the bleaching efficiency in turn. This indicated that bleaching efficiency increased with time and dosage up to the point of levelling off, which is better determined by optimization. Statistically, the D_{FB} was 3, D_{FW} was 7, F has a value of 269.15. A commendable high value showing a good variable relationship, P has a value of 1.37×10^{-7}, which, was relatively smaller than the P_C value of 0.05 in the 95% confidence interval. The Bonferroni-Holm Posthoc significance test of CR at various times for weight is shown in Table (6). The CR for the various time used were all significant with adsorbent weight.



(a)

(b)

(c)

Figure 6: Variation of Bleaching Efficiency with (a) Time (b) Temperature (c) Adsorbent Weight

Optimization of Variables

MINITAB Copyright © 2019 software was utilized to optimize the combined effect of bleaching temperature (X_1), time (X_2) and adsorbent dosage or adsorbent weight to oil volume ratio (X_3) on bleaching efficiency (Y), using the data range of the experiments. In the 95% confidence interval, the highest probability factor p was 0.006, which was less than

0.05 (showing model suitability), the standard error was 0.136565% and the R^2 value was 0.9983. The F value of 18.434 showed the significance of the model in the ANOVA analysis. The optimum Regression Equation for Y is given in Eq. 8. The adsorbent weight to oil volume ratio seems to have more effect than others due to its coefficients.

$$Y = 46.5515 - 0.4770 X_1 - 26.05 X_3 + 0.5563 X_2 + 5.000 (X_3)^2 - 0.09 X_1X_3 \quad (8)$$

The optimum parameters obtained are the temperature of 140 °C, a contact time of 45 minutes, the adsorbent weight of 2 g to crude palm oil ratio of 20 ml and bleaching efficiency of 99%.

Table 4: Bonferroni-Holm Posthoc Significance Test for the Effect of Time on CR at various Adsorbent Weights.

Group 1	Group 2	Critical	P	Significant
Time	CR at 2 g	0.0083	0.00000492	Yes
Time	CR at 1.5 g	0.0100	0.00000742	Yes
Time	CR1 at 1.0 g	0.0125	0.00002340	Yes

Table 5: Bonferroni-Holm Posthoc Significance Test for the Effect of Temperature on CR at various Adsorbent Weights.

Group 1	Group 2	Critical	P	Significant
Temperature	CR at 1.0 g	0.0083	0.000878	Yes
Temperature	CR at 1.5 g	0.0100	0.000879	Yes
Temperature	CR at 2.0 g	0.0125	0.000880	Yes

Table 6: Bonferroni-Holm Posthoc Significance Test for the Effect of Weight on CR at various Bleaching Time.

Group 1	Group 2	Critical	P	Significant
Weight	CR at 90 mins	0.0083	0.0000901	Yes
Weight	CR at 60 mins	0.0100	0.0001170	Yes
Weight	CR at 45 mins	0.0125	0.0001690	Yes

Utilization of Optimum Conditions

An experimental run was carried out using the optimum conditions to validate the predicted optimum values. Table 7 gives the optimum experimental results obtained. The optimum experimental value of 98% bleaching efficiency agreed closely with that obtained from the theoretical optimization with a percentage deviation of -1 % which, maybe due to experimental and environmental factors. The highest initial percentage reduction of 95% with a percentage deviation of -4% from the optimum showed that the experimental procedure was implemented efficiently. The optimum percentage colour reduction of 98% achieved competes with some commercial adsorbents bentonites by Kalidikalam *et al.*, [16] and kaolinites by Okafor *et al.* [18]. Crude palm oil bleaching with activated beans husks achieved results comparable to other substituted adsorbents reported by Raji *et al.* [20] and Lau *et al.* [21].

Table 7: Values obtained using Optimum Parameters

Parameter	Optimal Values
FFA	1.414 ml.mol/g
PV	1.026 ml.mol/g
Carotene	2.094
Absorbance	0.011
% Colour Reduction	98.00 %

Adsorption isotherms

From Olufemi and Otolorin [37] with Itodo and Itodo [38], the linearized Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherms were adapted to probe the sorption processes and are expressed in Eqs. (9) to (14).

Linearized Freundlich isotherm:

$$\ln q_e = \ln K_f + (1/n) \ln C_e \quad (9)$$

Linearized Langmuir Isotherm:

$$1/q_e = 1/q_m + 1/(q_m K_L C_e) \quad (10)$$

Linearized Temkin Isotherm:

$$q_e = (RT/b_T) \ln A_T + (RT/b_T) \ln C_e \quad (11)$$

Linearized Dubinin–Radushkevich isotherm:

$$\ln q_e = \ln q_D - 2B_D RT \ln (1 + 1/C_e) \quad (12)$$

$$E_D = \sqrt{1/2B_D} \quad (13)$$

$$q_e = (C_o - C_e)V/W \quad (14)$$

For each isotherm, the standard error of regression S, a standard error of the predicted dependent variable y for each independent variable x in the regression was evaluated using Eq. (15).

$$S = \sqrt{\frac{1}{(n-2)}\left[\sum(y-\bar{y})^2 - \frac{[\sum(x-\bar{x})(y-\bar{y})]^2}{\sum(x-\bar{x})^2}\right]} \quad (15)$$

where the mean values of x and y are $\bar{x}$ and $\bar{y}$, respectively. Also, ε_H is the highest error of prediction and ε_L is the lowest error of prediction given by Eq. (16).

$$y - \bar{y} = \varepsilon_H \ or \ \epsilon_L \ where \ \varepsilon_H > \varepsilon_L \quad (16)$$

C_o is the initial oil pigment concentration (ml), A_T is the Temkin isotherm equilibrium binding constant ($L.mol^{-1}$), b_T is the Temkin isotherm constant (J/mol), q_e is the quantity of colour pigments adsorbed at equilibrium ($mg.g^{-1}$), V is the solution volume (ml), W is the weight of solution (g), C_e represents the equilibrium concentration of mixture ($mg.L^{-1}$), K_F is the Freundlich equilibrium constant which signifies adsorptive capacity, K_L is the Langmuir constants ($mg.g^{-1}$), n is the Freundlich constant which represents adsorptive capacity, B_D relates to the free energy of adsorption per mole of coloured oil pigment in the solution ($mol^2.kJ^2$), q_D is the Dubinin–Radushkevich isotherm constant, which relates to the degree of sorbate sorption on the sorbent surface ($mg.g^{-1}$), E_D is the apparent energy of adsorption ($kJ.mol^{-2}$), q_m is the theoretical isotherm saturation capacity ($mg.g^{-1}$), R is the Universal Gas Constant ($J.mol^{-1}.K^{-1}$). At the same time, T is the absolute temperature (K). The Freundlich isotherm results are presented in Table (8). The linearity of the plot pointed to the fitness of adsorption on the adsorbents. From the adsorption isotherm, the quantity of colour pigments adsorbed was proportional to the change in solute concentration in the solution. The value of n depicted that the activated beans' husks were an excellent adsorbent since it was below 0.5. The K_f value indicates the decolorizing power or activity of the adsorbent material for any solute. The Freundlich isotherm model suitably described the adsorption data for all the samples investigated with the highest R^2 value of 0.9901 and very low S, ε_H and ϵ_L values of 0.000355, -0.000264 and -0.0280136 to establish the statistical adequacy of the observation. The K_f values increased with temperature, indicating increased access to adsorption sites. The Langmuir isotherm fitted the adsorption to some extent, as shown in Table 9 with low errors. In Table 10, the Temkin model is mainly used for heterogeneous surface energy systems. The error evaluation was moderate. The constants b_T and A_T indicate the heat of sorption and Temkin isotherm equilibrium binding constant, respectively. The linear relationship of the plot depicted the representation of the adsorption on the adsorbents. The Dubinin-Radushkevich isotherm evaluation with few errors is shown in Table 11. The model is mainly used to determine the apparent energy of heterogeneous surface systems. Also, the linear nature of the plot showed the adsorption relationship type on the adsorbents. The value of E_D > 8 kJ.mol^{-1} revealed chemisorption. Comparing the isotherms based on their R^2 values indicated that the Freundlich isotherm gave the best fit and is most favoured for the adsorption. The Temkin and Dubinin-Radushkevich constants showed certain energy parameters. The Dubinin-Radushlkevich Isotherm is most general because its deviations are not based on ideal assumptions such as eqi-potential of sorption sites and the absence of steric hindrances between sorbed and incoming particles and surface homogeneity on the microscopic level. The highest S value was 4.3117 mg.g^{-1} showing the statistical adequacy of the isotherms evaluation.

Table 8: Freundlich Isotherm Parameters

Isotherm Model	Parameter	Temperature (ºC)				
		50 ºC	80 ºC	110 ºC	140 ºC	170 ºC
Freundlich	K_f	0.4302	0.5141	0.5682	0.6134	0.694
	N	-1.2838	-1.0706	-1.1945	-0.9763	-1.1384
	R^2	0.979000	0.985000	0.988800	0.990100	0.980000
	S (mg.g^{-1})	0.016659	0.007269	0.008667	0.000355	0.000567
	ε_H (mg.g^{-1})	0.020133	0.000190	0.006889	-0.000264	0.000060
	ε_L (mg.g^{-1})	-0.00592	0.000404	-0.00490	-0.028014	-0.00010

Table 9: Langmuir Isotherm Parameters

Isotherm Model	Parameter	Temperature (ºC)				
		50 ºC	80 ºC	110 ºC	140 ºC	170 ºC
Langmuir	q_m	0.005	0.014	0.032	0.038	0.048
	K_L	-0.4892	-0.209	-0.341	-0.315	-0.482
	R^2	0.9670	0.9780	0.9881	0.9888	0.9790
	S (mg.g^{-1})	4.3117	0.6387	3.2250	0.1084	0.01136
	ε_H (mg.g^{-1})	-0.1120	-0.02815	0.036648	0.01404	0.001605
	ε_L (mg.g^{-1})	-5.4974	-0.84335	-7.38776	-0.12217	-0.012605

Table 10: Temkin Isotherm Parameters

Isotherm Model	Parameter	Temperature (ºC)				
		50 ºC	80 ºC	110 ºC	140 ºC	170 ºC
Temkin	b_T	0.045	0.052	0.043	0.0367	0.052
	A_T	23.41	21.75	19.56	18.85	19.32
	q_e	114.53	127.89	139.647	145.85	151.23
	R^2	0.9702	0.9715	0.9789	0.9800	0.9743
	S (mg.g^{-1})	0.000133	0.000249	0.000593	0.0000248	0.0000227
	ε_H (mg.g^{-1})	0.000073	0.000173	-0.00016	-0.000110	0.0000077
	ε_L (mg.g^{-1})	0.000096	-0.000082	-0.00037	-0.000078	-0.000022

Table 11: Dubinin-Radushkevich Isotherm Parameters

Isotherm Model	Parameter	Temperature (ºC)				
		50 ºC	80 ºC	110 ºC	140 ºC	170 ºC
Dubinin-Radushkevich	q_e	0.005	0.014	0.032	0.038	0.048
	B_D	0.4892	-0.209	-0.341	-0.315	-0.482
	E_D	28.98	30.75	37.51	40.86	38.52
	R^2	0.8260	0.8337	0.8701	0.8827	0.8797
	S (mg.g^{-1})	0.044992	0.021035	0.008743	0.000499	0.00014
	ε_H (mg.g^{-1})	0.128100	0.077824	0.010365	0.001733	0.04090
	ε_L (mg.g^{-1})	0.063740	0.045567	-0.00169	0.001053	0.040018

Table 12. Pseudo-first Order Kinetic Model Parameters

Kinetic Model	Parameter	Temperature (ºC)				
		50 ºC	80 ºC	110 ºC	140 ºC	170 ºC
Pseudo-first order	K_1 (min^{-1})	-0.0156	-0.1164	-0.0994	-1.3678	-1.3966
	q_e (mg.g^{-1})	6.9300	7.1950	6.9989	7.2300	8.6700
	R^2	0.9803	0.9827	0.9824	0.9883	0.9001
	S (mg.g^{-1})	0.000428	0.00449	0.0190	0.00511	0.00321
	ε_H (mg.g^{-1})	-0.0011	0.0044	0.0149	0.0016	0.0026
	ε_L (mg.g^{-1})	-0.0023	-0.0018	-0.0104	-0.0051	-0.0014

Table 13. Pseudo-second Order Kinetic Model Parameters

Kinetic Model	Parameter	Temperature (ºC)				
		50 ºC	80 ºC	110 ºC	140 ºC	170 ºC
Pseudo-second order	K_2 (g.mg^{-1}.min^{-1})	0.12060	0.00426	0.00308	0.00225	0.00180
	q_e (mg.g^{-1})	8.390	9.436	10.790	11.660	9.930
	R^2	0.9907	0.9934	0.9953	0.9998	0.9978
	S (mg.g^{-1})	0.37176	0.6401	0.2699	0.0230	0.0027
	ε_H (mg.g^{-1})	0.1980	0.5160	0.2180	0.0180	0
	ε_L (mg.g^{-1})	-0.2990	-0.3400	-0.1430	-0.0125	-0.0030

Table 14. Elovich Kinetic Model Parameters

Kinetic Model	Parameter	Temperature (ºC)				
		50 ºC	80 ºC	110 ºC	140 ºC	170 ºC
Elovich	α (mg.g^{-1}. min^{-1})	0.3287	0.4261	0.8198	1.1154	0.9570
	β (mg.g^{-1}. min^{-1})	0.4937	0.5840	0.4163	0.4081	0.5370
	R^2	0.9852	0.9870	0.9770	0.9900	0.9790
	S (mg.g^{-1})	0.0000114	0.000178	0.000493	0.0000189	0.00000875
	ε_H (mg.g^{-1})	-0.00014	0.000163	0.000109	-0.000075	0.0000718
	ε_L (mg.g^{-1})	-0.00017	-0.00006	-0.00052	-0.000046	0.0000579

Adsorption Kinetics

Eqs give the pseudo-first order, pseudo-second order and Elovich models adapted from Okafor et al., [18] as well as Olufemi and Nlerum [39]. (15), (16) and (17) respectively, where, q_t (mg.g^{-1}) is the quantity adsorbed at time t, while k_1, k_2, α and β are kinetic parameters.

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)\, t \tag{15}$$

$$t/q_t = (1/k_2 q_e^2) + t/q_e \tag{16}$$

$$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln(t) \tag{17}$$

Similarly, S, ε_H or $\epsilon_L$were evaluated for the kinetics.

The kinetic parameters evaluated from the slopes and intercepts of the kinetic equations' respective linear plots are shown in Tables 12 – 14 with minor errors. A comparison of the various kinetic plots based on their R^2 values indicated that the pseudo-second-order model (R^2 = 0.9998) best described the adsorption at all temperatures a$nd\ S, \varepsilon H, or\ \epsilon_L$values of 0.0230, 0.0180 and -0.0125 mg.g^{-1} established the statistical suitability of the kinetics. The pseudo-second-order rate constants (K_2) decreased, whereby the equilibrium capacity values (q_e) increased up to 140 ºC. The estimated equilibrium capacity value was within the range of the experimental data. The highest S value was 0.37176 mg.g^{-1}.

Conclusions and Recommendations

The results showed that producing activated carbon with good properties from local beans husks waste material is possible. A high carbonization temperature yielded carbon with high adsorption capacity, as temperatures below 500 ºC gave incomplete carbonization. The results of this work indicated the great potential of activated bean husks as adsorbents for removing color pigments from crude palm oil and finding a cheap substitute that can efficiently perform the bleaching process like bleaching clay or commercial bleaching agents, which has a negative impact on the environment. Optimization specified variables of 140 °C, 2 g adsorbent to 20 ml oil ratio of 10% and 45 minutes for adsorption. Theoretical optimum percentage colour reduction was 99%, which showed the experiments' adequacy that achieved 98%. From the isotherms, the acid-activated samples were highly influential in the adsorptive bleaching of palm oil. Dubinin-Radushkevich isotherm suggested chemisorption. The pseudo-second-order model emerged as the best fit suitable for the adsorption. The statistical error evaluation further improved the integrity of the data obtained. The results of this study indicated that bean husks served as an excellent adsorbent for palm oil refining and are recommended as a substitute or complement for industrial applications and further studies.

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