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Performance of Synthesized Rice Husk Ash (RHA-Based) Adsorbent as a Palm Oil Bleaching Material

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--- ***ABSTRACT*** ---

An adsorbent for palm oil bleaching was synthesized from incinerated rice husk ash (RHA). Powdered RHA was sieved and utilized for producing RHA absorbent using calcium hydroxide and calcium sulphate by the method of impregnation. The precursor solid was calcined at 200^{o}C for 3 hours, characterized using FTIR and XRF techniques and studied for its bleaching action on palm oil by maintaining the stirring rate and contact time while varying the catalyst loading.The SiO_2, P_2O_5 and CaO content were determined to be 49.765%, 9.52% and 30.216% respectively, with traces of K_2O, SO_3 and Al_2O_3. Absorption bands that appeared around 1055-1030cm^{-1}, 875 cm^{-1}were attributed to Si-O and Ca-O bonds respectively, while the intense band observed between 1330-1430cm^{-1} was assigned to O-H bending (in-plane) vibration.The absorbent proved effective for decolourizing palm oil.

KEYWORDS: *Rice Husk Ash, Adsorbent, Bleach, Palm Oil.*

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I. INTRODUCTION

Rice husks or (rice hulls) are hard protecting coverings of grains of rice. In addition to protecting rice during the growing season, rice husks can be put to use as building material, fertilizer,additives, insulator material, or fuel [1-3].

Rice husk ash (RHA)is a by-product obtained after incinerating rice husk. During milling of paddy, about 78%(weight of the paddy) is received as rice, broken rice and bran. Other 22% (weight of the paddy) is received as husk. This husk is used as fuel in the rice mills to generate steam for the parboiling process [2].

During the firing process, about 25%of the 75% organic volatile matter is converted into ash to give a product which is known as rice husk ash (RHA);which according to Wallheimer[3] contains 85% - 90% amorphous silica.

Mitani*and coworkers*[4], reported thatRHA constitutes a great environmental threat (damage to the land and the surrounding) to the area in where it is dumped. Ways of disposing them could be making commercial use of this RHA in order to obtain cheaper useful materials.

Crude palm oil product industry is one of the fastest growing in many oil-producing countries, with Malaysia taking the lead [5-6]. The production of palm oil is relatively complex but the current technology has given it a major boost. Extraction from themesocarp of the palm fruit involves a number of processes or stages in order to obtain refined and bleached palm oil. The most commonly used method is physical refining whichincorporates stages such as degumming, bleaching and lastly, deodorization. According to Chumeeand Jian[7], degumming the palm oil (during bleaching process) is the most important activity in palm oil refinery.

The (palm oil) bleaching process ought to be carefully done to the last point as it requires professional monitoring. For this reason, any unattended complications and imperfections may adversely affect the stages of the bleaching and subsequently, the finished product will be of low quality[5-7]. This is one of the majorcontributor, to the overall operational costs of any palm oil production plant. This is for the reason why the costs of the chemicals involved are very high, precisely the bleaching earth and the phosphoric acid.

Again, the effectiveness of the process depends on the correctness of the ratio of bleaching earth to the crude palm oil used. The sole purpose of the palm oil bleaching process is to absorb impurities in the crude oil, mostly saturated and unsaturated fats. The bleaching earth also neutralizes Free Fatty Acids-FFA, leading to the efficiency of the end-point stages and high quality finished palm oil[8].

Rice husk is a potential material, which is amenable for value addition. The usage of rice husk either in its raw form or in ash form is many. Most of the husk from the milling is either burnt or dumped as waste in open fields and a small amount is used as fuel for boilers, electricity generation, bulking agents for composting of animal manure, etc [9].

According to Prasad *eta.l*[10], RHA is the most wanted material for steel industries, ceramic industry and for the manufacture of refractory.Basha*and* co-workers[11] examined the possibilities of improving residual soilproperties by mixing RHA and cement in suitable proportions as stabilizingagent, and in additionIndian Space Research Organization has successfully developed a technologyfor producing high purity silica from RHA that can be used in silicon chipmanufacture [9-11]

Naito [12], introduced a low cost technology for controlling insect pests inSoya beans by using RHA, the insects are irritated by the high levels ofsilicon and the needle like particles.

Saha*et al*. [13], studied the possibility of using RHA for manufacturingactivated carbon, and confirmed its usefulness in water purification.

Attempts have been made to utilize RHA in vulcanizing rubber. RHA has beenshown to offer advantages over silica as a vulcanising agent for ethylenepropylene-dieneterpolymer (EPDM), and is recommended as diluents fillerfor EPDM rubber [14].

There are two distinct stages in the decomposition of rice husk viz carbonization and decarbonation. Carbonization involves the releases of combustible gas and tarwhen decomposition of volatile matter in rice husk at temperature greater than 300°C takes place. Decarbonation, is the combustion of fixed-carbon in the rice husk char at higher temperature in the presence of oxygen [15]. The melting temperature of RHA is estimated as 1440°C, that is, the temperature at which silica melts [9,14-15].

According to Stroeven*et al*. [16], rice husk ash contains 87-97% of silica (SiO_2) with small amount of alkalis and other trace elements. Based on temperature range and duration of burning of the husk, crystalline and amorphous forms of silica are obtained.

Linoleic acid is one of the two essential fatty acids that humans require [17-18] Palm oil is also high in vitamin K and dietary magnesium. It is rich in minor components which have nutritional attributes with about 500-700ppm of carotene consisting mainly of α and β carotenes that constitute 90% of the total carotene [17-18].

In the purification, decolourisation and stabilization of vegetable oils, the bleaching step is a critical step. Bleaching of vegetable oils is important for producing a light coloured oil of acceptable quality. This improvement in colour is due to the removal of organic compounds such as carotenoids, especially β-carotene, and their derivatives, xanthophylls, chlorophyll, pheophytin, tocopherols, gossypol, and their degradation products, which impart undesirable colour to the oils [17] Bleaching is a process which involves the removal of pigments, impurities, trace metals and high molecular oxidative component from fats and oil [5-6, 17-18]. The removal of these substances is essential in the refining of oils as it improves the stability, appearance and the sensory quality of the oil [20-21].

The process is aimed at removing coloured material, impurities such as gums (phosphatides), traces of metal and free fatty acids which may produce oxidation products leading to degeneration and short life of the finished product [22]. It is important to have proper refining process in order to produce high quality finished product with specified quality range that meet user's requirements. There are basically two types of refining processes available in the vegetable oils industries, namely, chemical and physical refining [23].

Rossi *et al.* [24] is of the view that, among these stages, bleaching is the most critical phase since it helps to improve the appearance, flavour, taste and stability of the final oil products.

Activated carbon has been used in bleaching oil, but its use is limited due to the high operation costs, which is a major economic consideration in any production process [24,32]and lastly, synthetic silicatesare used in edible oil bleaching, largely in wet bleaching with a focus on selectively removing phosphatides, trace metals and soaps. Although they have a moderate capacity for pigment removal, they are used in combination with bleaching clay and due to the synergic action the amount of bleaching clays is reduced [24-25]

The general bleaching process is carried out at temperature in the range of 80-120°C and contact time ranging from 20 to 40 minutes under vacuum or nitrogen. The dosage of bleaching earth can vary depending on both the process and oil type. Chemical refining uses 0.5-2% on a weight basis while physical refining uses 0.25-2%. However for darker oils, 2-4% bleaching earth may be used to meet final colour requirements [22]. After bleaching, the bleaching agent is removed through vacuum filtration.

II. EXPERIMENTAL

Sample Collection

Rice husk sample was collected from KK Parboiled Rice Company, along Keystone Bank KantinDaji Area, Sokoto, in a polythene bag; Palm oil was bought from trade fair junction in a 5litre gallon and bothwerestored in the laboratory before required analysis.

Ashing

Rice husk (120g) each was transferred to 5 crucibles and incinerated for approximately 48 h in blast furnace. The temperature was within the range of 400-650^{0}C**.** The ash collected was grounded and sieved through BS standard sieve size 75µm.

Preparation of RHA Adsorbent

The RHA adsorbent was prepared by transferring RHA powder (45g) into an empty beaker followed by the addition of calcium hydroxide (5g) and calcium sulphate (1g) tothe mixture after which deionized water (100 ml) was added. The beaker was placed on a magnetic stirrer set at 100rpm with continuous stirring until slurry was obtained.

Heat Treatment/Calcination

The precursor (solid residue) was transferred to a crucible and heated in a blast furnace at 200^{0}Cfor 3 hours. The solid absorbent was characterized using FTIR and XRF analyses.

Palm Oil Bleaching Using the Prepared RHA Adsorbent

Four (4) beakers containing palm oil (100ml)each were arranged and labelled A, B, C and D (Fig. 1) . To the first (beaker A), 2g of RHA adsorbent, the second (beaker B),5g of RHA adsorbent, the third (beaker C), 10g of RHA and the fourth (beaker D) served as the control.Fig. 1 (below) depicts the samples on amagnetic stirrer.
The magnitude of stirring was maintained at120 revolutions per minutes and contact time of 60 minutes.

Sample A	Sample B	Sample C	Sample D
RHA 2wt%,	RHA 5wt%,	RHA 10%wt	Fresh Sample
Palm Oil (100ml)	Palm Oil (100ml)	Palm Oil (100ml)	Palm Oil (100ml)

Fig. 1: Palm oil samples containing different catalyst loading after magnetic stirring.

III. RESULTS

Results of experimental methodology obtained from the work is presented in Tables 1-2 and Figures 1 and 2.

3.1 Result of X-ray Fluorescence (XRF) Spectroscopy

The result of X-ray fluorescence (XRF) analysis of RHA is present in the Table 1.

Table 1: Result of X-ray Fluorescence (XRF) Analysis of the Prepared RHA Adsorbent.

Element/Oxide	Composition (wt%)
MgO	3.217
Al_2O_3	0.876
SiO_2	49.765
P_2O_5	9.525
SO_3	3.313
K_2O	2.231
CaO	30.216
Others* (Not L.O.I)	0.901

LOI=Loss on Ignition

Table 2: The prominent peaks Realized in the FTIR Spectra of the RHA Absorbent

Absorption (cm^{-1})	Description	Expected Compd./ Functional Group
1420	Broad intense	N-H Bond/Stretching
1054	Broad intense	C-C bond/Stretching
875	Weak narrow	Si-O

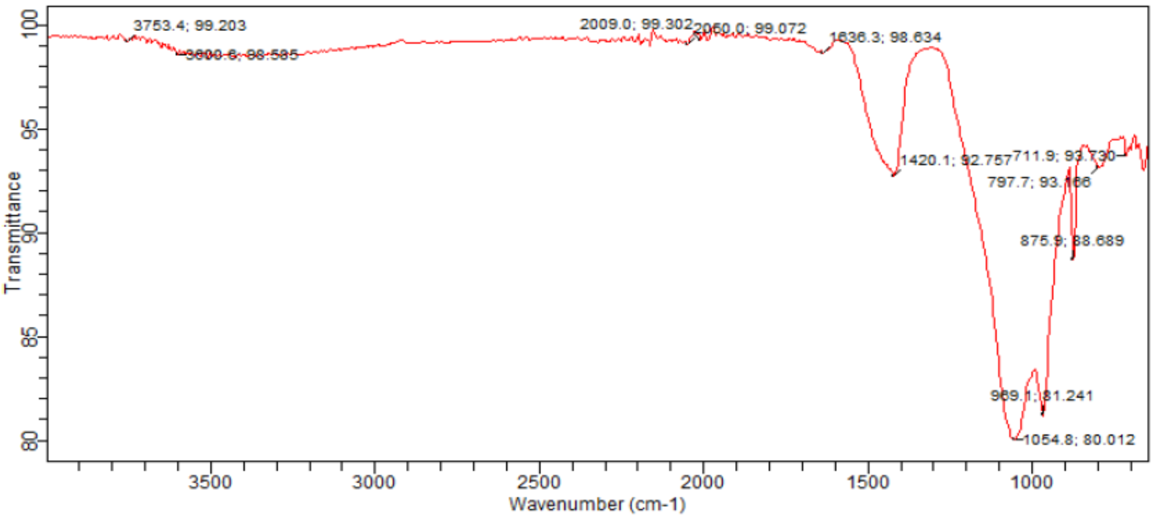

Fig. 1: FTIR Spectra of the RHA Adsorbent

IV. DISCUSSION

The result presented in Table 1showed the available oxides in the rice husk ash adsorbent.X-ray Fluorescence Spectroscopy (XRF) is a non-destructive analytical technique that determines the chemical composition of materials, particularly in the investigation of solid materials and stabilizing their elemental compositions. Although there are a number of oxides and atoms in trace quantities, impurities ranging from Mn_2O_3 (0.327wt%), Fe_2O_3 with (0.303wt%), Cl (0.105wt%), ZnO (0.0078wt%) TiO_2 (0.034wt%), SrO (0.009wt%), Na_2O (0.000wt%), and Cr_2O_3 (0.000wt%) amounted to 0.901wt%.Presence of these impurities is usually observed in the XRF technique of analysis due to inherent binded compounds from the precursor materials [29]. It is clear that silica content realized in the bleach material dominated the others by far. This could be attributed to the fact that silica does not degrade or decompose during combustion and corresponds to the report of [31-32]. Accordingly, the percentage availability of P_2O_5 (9.525) is also reasonable, next to CaO (30.216). Reports by [33] claimed that the principal oxides inrice husk ash are those of metals with traces of non-metallic oxides like SO_3 which is only 3.313% abundant.

The pattern of peaks is attributable to the active groups (absorption bands); in order to identify the major functional groups present in the sample, FTIR spectroscopy was employed (Table 2).The medium-intensity peak observed around 1420cm^{-1}(between 1330-1430cm^{-1}) can be attributed to O-H bending (in plane) vibration. The band at 989cm-1 could be attributed to phosphorus (P-OR) 900-1050 (stretch) as reported by Galvan-Ruiz *et al.*[27]; Launer and Barry, [28]. The strongest band in the spectra observed around 1054cm^{-1} is attributed to Si-O. The absorption fall within 1055-1030cm^{-1} described for Si-OCH$(CH_3)_2$ by [28] in infrared analysis of organosilicon compounds; spectra-structure correlations. Silicon-alkoxy compounds show a well-defined sharp, strong band (doublet in some cases) in the 1110-1000 cm^{-1} range. However, the band is apt to be masked by strong Si-O-Si absorption if siloxane is present; in such cases, the alkoxy group is often identified using other bands.

The weak narrow band that appeared around 875cm^{-1} is due to the possible presence of silicon carbide (ceramic) material in the adsorbent. Acording to [28], all forms of silicon carbides (SiC) will show a strong absorption at or near 800cm-1. Amorphous silicon nitride (Si_3N_4) also shows a strong band around 840cm^{-1}

The catalyst loading in the different palm oil samples. It could be observed that the rate of bleaching increased with increase in the catalyst loading (Fig. 1). This correspond to the report of Alhassan*et al.* [29], that catalyst loading, contact time and rate of stirring per minute affects the activity of catalysts.

Effect of Adsorbent Loading

Variation in the deepness of the palm oil colours in each flask displayed in Figure 1 is obvious. Appearance of colour is due to the presence of chromophores (colour bearing groups) in the compounds. Accordingly, presence of bleach materials fade out the chromophores by deactivating them, thereby decolourizing them[30-32].

The differences in the hues observed in samples A B C and D could be due to the variation in the adsorbent loading from 2wt%, 5wt% and 10wt% since the stirring rate and contact time were maintained.

V. CONCLUSION

Palm oil bleaching material was successfully prepared from rice husk (paddy) mostly recognized as waste materials. The absorbent proved effective for palm oil decolourization and there was chromophore deactivation.

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