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Analysis of Local Adsorbents for the Capture of Greenhouse Gas and Acid Gases

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Abstract:

The use of adsorbents for separation of carbon dioxide from greenhouse and acid gases is an important process in separation technology. Conventional adsorbents such as zeolites are used for separation of carbon dioxide from these gases. In the present work, the adsorption for separation of carbon dioxide in local adsorbents such as coconut shell and palm kernel shell were studied using Brunauer-Emmett-Teller (BET) Analyser, X-Ray Florescence (XRF), density apparatus, and thermogravimetric analyser DTA (TGA-DTA). The above-named equipment was used for the estimation of corresponding surface area and pore volume, elemental and oxide composition, bulk density and thermal stability, respectively. Palm kernel shell activated charcoal (PKSAC) and coconut shell activated charcoal (CSAC) were specifically investigated to ascertain their adsorption capacity and characteristics using some important properties such as surface area and bulk volume. Findings show that the activated carbon from palm kernel shell has a surface area of 521.864 m^2/g, a pore volume of 0.472 cc/g, and a moisture content of 2.4%, while the activated carbon from coconut shell has relatively lower values of surface area of 377.332 m^2/g, pore volume of 0.342 cc/g, and moisture content of 2.1%. Also, TGA analysis results show TGA profile (Micrographs) and mass by weight values of PKSAC and CSAC are 80% and 75% respectively. It can further be deduced from these results that PKSAC has relatively larger surface area, and thus a better absorption capacity than CSAC. In addition, the PKSAC indicated a better thermal stability than CSAC, with moisture content values for both samples mostly similar, with slightly larger values for PKSAC. Similar trends in pore volume behaviour are also noted. Overall, the PKSAC had better surface areas, pore volume and cumulative surface areas than the CSAC, and by implication would perform more efficiently as an absorbent for carbon dioxide (CO2) and methane (CH4) tests.

Keywords — Local Adsorbents, Carbon Dioxide Capture, Greenhouse Gases, Acid Gases.

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I. INTRODUCTION

Among greenhouse gases (GHGs), CO2 is considered the biggest contributor to current global warming [4] and its concentration in the atmosphere continues to rise as fossil fuel consumption continues to widen globally [1].

Gas-fired power generation facilities are the biggest point source of atmospheric CO2 [1]. Carbon dioxide can be found in greenhouse and acid gases and one technology to remove them from these types of gases is adsorption technology. Thus, adsorption technologies can play a key role in the mitigation of global warming.

There has been much interest towards the development of technologies for removal of carbon dioxide recovered from greenhouse and acid gases. Absorption process using solvents such as Amine is a common technology for addressing, however, adsorption process is a more efficient process,

especially, if one requires minimum concentration of this impurity in the source gases.

Conventional adsorbents exists but inspite of their existence, alternative adsorbents such as palm kernel and coconut shell should be considered as acceptable, locally sourced alternative, and they can be found in countries like Malaysia, Nigeria, Brazil, and many more [3].

In this work, we investigate the adsorption characteristics of palm kernel and coconut shell – based adsorbents for carbon dioxide separation from greenhouse and acid gases [1, 7, 8].

II.   MATERIALS AND METHODS

A. *Coconut Shell: Properties and Applications*

The properties of coconut shell include physical and mechanical aspects that make it a versatile material with their particles being studied for their mechanical properties like tensile strength, tensile modulus, flexural strength, impact strength, hardness, and water absorption. Additionally, coconut shell charcoal is widely used to produce active carbon, known for its effectiveness in removing impurities, making it valuable in purification industries [1].

In terms of concrete applications, coconut shell concrete exhibits better workability due to its smooth surface, with properties like compressive strength, flexural strength, splitting tensile strength, and impact resistance comparable to normal and other lightweight aggregate concretes. Moreover, coconut shell concrete has been found to have high bond strength, making it suitable for structural applications and potentially as a building material in concrete, similar to other lightweight aggregates [4].

The application of coconut shells includes various uses such as producing coconut shell charcoal, coconut shell activated carbon, and coconut shell powder. Coconut shell charcoal is utilized as a domestic and industrial fuel, particularly in producing activated carbon, which is superior to other variants and widely used in industries like laundries, blacksmithing, and goldsmithing [23].
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Additionally, coconut shell powder finds applications in manufacturing of mosquito coils, incense sticks, plywood, and resin glue due to its uniform quality and resistance to water and fungal attacks. Moreover, coconut shells can be used in horticulture during soil amendment, composting material, and seed starting mix, providing benefits like improving soil quality, enhancing water retention, and promoting healthy plant growth [16].

B. *Palm Kernel Shell: Properties and Applications*

The properties of palm kernel oil include being a lauric type similar to coconut oil, producing hard soaps that lather well, and having a high content of lauric acid. Palm kernel oil is significantly harder at temperatures below 20°C but melts faster above room temperature than palm oil, with a melting point about 10°C lower than that of palm oil. It contains minor amounts of cholesterol, tocopherols, tocotrienols, and phytosterols, with a deep red colour due to a high concentration of carotenoids. The phytonutrient content of kernel oil is lower than that of palm oil [14].

Palm kernel shell, the outermost part of the seed, is a protector to the seed and is thick and brown/black wood-like in structure. It is a by-product of the production of palm kernel oil and palm oil, with properties like solid density, porosity, specific gravity, specific heat capacity, moisture content, and angle of repose varying depending on geographic location. Using palm kernel shell as a filler material in polymer composites can modify the properties of the filler and enhance the characteristics of the composite material [15].

The edible seed of oil palm fruit is referred to as a palm kernel. Palm fruit yields two distinct forms of oil, each with unique properties. The first oil is called palm oil, and it comes from the fruit's fleshy, fibrous outer layer. Palm kernel oil is made from the edible kernel [14]. Being the outermost portion of the seed, the palm kernel shell serves as protection for the seed. Before the edible portion is

revealed, the shell must be cracked. The oil palm tree is thought to have evolved in the tropical rain forests of West Africa. The nations that make up the equatorial belt that are part of the Oil Palm (Elaeis guineensis) belt are Ghana, Nigeria, Togo, Cameroon, Cote d'Ivoire, Liberia, Sierra Leone, Congo, and Angola [16].
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The application of palm kernel shell (PKS) is diverse and extensive across various industries and sectors. PKS, a by-product of palm oil production, serves multiple purposes, demonstrating its versatility and sustainability. In the natural biomass energy industry, PKS is highly valued as a fuel source due to its high calorific value of approximately 4000 Kcal/kg and low ash content, making it an appealing renewable energy option. Moreover, PKS finds application as an adsorbent for treating heavy metal ions, providing a cost-effective and environmentally friendly method for water treatment. In addition to these uses, PKS is employed in agriculture and industry for activities such as composting, producing activated charcoal, and creating biochar. This wide range of applications underscores the significance of PKS as a valuable resource with beneficial implications for various sectors [1].

Palm kernel shells have been put to several application, both domestically and industrially due to its abundance in Nigeria. Its applications ranging from biomass, energy storage, bio-fertilizer, to super-capacitor electrode [5][6]. Through the use of the sol–gel technique, this work synthesized amorphous mesoporous silica from PKSA agricultural bioresources [3]. Many researchers and scientists have used PKS to substitute conventional normal weight aggregates (NWA) as lightweight aggregates (LWA) in motorway construction, essential elements and others. Its combined benefits include lower costs for prized amorphous silica and a reduction in disposal and pollution issues. When compared to alternative extraction techniques, the sol-gel approach yields more silica, uses less energy, and densifies at a lower temperature [11;14];15].

When compared to other biomass such as coconut shell, wheat husk, and rice husk, PKSA as a source of silica has a greater net calorific value (LHV), indicating big energy value and higher ash content [16;17;18]. Using XRD, XRF, SEM/EDX, FTIR, and TGA methods, the produced amorphous mesoporous silica from palm kernel shell ash (PKSA) has been studied. Table 1 shows the chemical composition of raw husk, PKSA and extracted silica in percentage [3].

TABLE I: **Chemical composition of raw husk, PKSA and extracted silica**

OXIDES	RAW HUSK	BEFORE SYNTHESIS	AFTER SYNTHESIS
ORGANIC MATTER	42.2	-	-
S_iO_2	13.65	56.76	96.83
AL_2O_3	9.18	8.58	0.0
FE_2O_3	1.81	0.91	0.17
CAO	13.21	12.57	0.43
MGO	6.54	5.45	0.17
SO_3	0.84	0.71	0.0
P_2O_5	4.37	4.21	0.0
K_2O	6.48	9.19	1.43
NA_2O	1.71	1.62	0.97

C. Carbon Capture System

The benefits and drawbacks of current carbon capture systems and porous materials include:

1. Adsorption technology is favoured for CO2 capture in post-combustion conditions such as low pressure, mild temperatures, and low carbon dioxide concentration, where implementing absorption techniques will result in high operating costs [18].
2. Solid porous materials offer high uptake capacity, easy recovery process, resistance to humid conditions, and high stability [19].
3. Carbon capture and storage (CCS) technologies are focused on reducing the amounts of CO_2 released into the atmosphere by separating it from other gases, compressing, transporting, and

finally storing the captured CO_2 far away from the atmosphere, avoiding any leakage back into the ecosystem [16]

4.   CCS can help maintain industrial production and economic growth while reducing emissions [3]

Drawbacks of current carbon capture systems and porous materials:

1.   The development of porous materials for carbon capture has relied mostly on trial-and-error approaches or serendipitous discoveries, leading to slow progress of this research field [13]

2.   The high costs associated with CCS technologies have limited large-scale annual capture and storage capacity to only about 0.1% of global CO_2 emissions [18]

3.   Questions remain about how effective carbon capture and storage (CCS) really is, alongside low adoption rates due to a limited business case and lingering public concerns about safety [26]

4.   The most studied adsorbents include carbon, zeolites, and metal-organic frameworks (MOFs), each with their own advantages and limitations [12]

D. *Potential Adsorbents and Adsorption Parameters for Carbon Dioxide Capture*

Carbon dioxide (CO2) capture is an important strategy to reduce the amount of CO2 released into the atmosphere. Here are some potential adsorbents and adsorption parameters for CO2 capture

Potential Adsorbents:

1.   Carbon-based materials such as activated carbons, carbonaceous materials, and biochar-based adsorbents [9]

2.   Zeolites, calcium oxides, hydrotalcites, organic-inorganic hybrids, and metal-organic frameworks [6]

Adsorption Parameters:

1.   Equilibrium CO2 capacities
2.   Adsorption-desorption kinetics
3.   Operating windows
4.   Stability
5.   Regenerability
6.   Morphology
7.   Surface area
8.   Functionality
9.   Wall thickness.temperatures

E. *Methodology for Determination of the Particle size distribution of the Activated Carbon*

(1) PROCEDURE – SAMPLE PREPARATION

The sample was weighed into the sample cell. The filled sample cell bulb was inserted into the heating mantle. The clamp was placed around the mantle so that the sample cell was held firm. The sample cell stem was inserted into the sample preparation station. The knurled ring was tightened by turning it clockwise to secure the sample cell in the preparation station. After securing the sample cell(s) in the preparation station, out gassing was initiated by entering the control panel menu on the instrument. The outgassing temperature was set to 2500C and the system was set to start degassing for 3hr and the heater was switched on. When the sample has out gassed for 3hours the heating mantle was turned off, the heating mantle and the sample cell was allowed to cool. Once the heating mantle has cooled, the outgas station and the sample were unloaded and removed. the sample cell was reweighed to determine the post out gas sample weight.

(2) PROCEDURE – Sample Analysis

The internal upper mark was filled with liquid nitrogen, the sample cell containing an out gassed and weighed sample was placed into the analysis station to be used for analysis. All the fields/selections on the start analysis ''Sample'' menu was completed. Point selection and tagging on the start Analysis ''Points'' menu was also completed. Fields on the start Analysis ''Equilibrium'' menu was completed. Field defaults was to be used for BET measurements. When all fields are completed on the start Analysis Menu.

III.   RESULTS

A. *Surface Area of Activated Coconut Shell (CSAC) and PKSAC*

(a)

Figure 1: Brunauer-Emmett-Teller Analyser

(b)

Figure 1: Muffle furnace, used for heating test samples to extremely high temperatures

B. *Determination of the Bulk density of the Activated Carbon Sample Procedure*

A quantity of powder sufficient to complete the test was passed through a sieve with apertures greater than or equal to 1.0 mm, if necessary, to break up agglomerates that might have formed during storage. This was done gently to avoid changing the nature of the material. The 100g of sieved sample weighed with the accuracy of 0.1% was put into a dry graduated cylinder of 250 ml (readable to 2 ml). The powdered sample was levelled carefully without compaction and the unsettled apparent volume (V_0) was read to the nearest graduated unit. The bulk density in g per ml by the relationship (eq. 1):

$$Bulk\ Density = \frac{m}{V} \qquad (1)$$

where:

m = required mass
V_0 = unsettled apparent volume

The unsettled apparent volume of the powdered sample was between 150ml and 250ml, so, 100g was used for accurate results. The results of the bulk density of the activated carbon were recorded The results of the BET analysis for CSAC and PKSAC were presented in figure 2 showing different parameters that were determined.

1) Comparing the Surface Area of Coconut Shell (CSAC) and Palm Kernel (PKSAC): A The surface area of activated coconut shell was measured at 377.332 m^2/g, but that of active palm kernel shell was 521.864 m^2/g, as shown in Figure 2. It was suggested that the activated palm kernel shell has a larger surface area than the active coconut shell [20].

2) Since the surface area of activated carbon is a critical factor, PKSAC's larger surface area suggested that it would perform better than CSAC in terms of carbon's ability for adsorption. A bigger surface area indicates more active sites on the carbon surface, which can improve the effectiveness of adsorption. The activated palm kernel shell in this case has a bigger surface area

than the active coconut shell, which might mean that it has better adsorption capacities.

The two samples' cumulative surface areas (Figure 5) demonstrate that PKSAC outperformed CSAC since the former's cumulative surface area was larger. Hence, the amount of CO2, methane or any other gas that would be adsorbed relies on the exposed surface area, the location of the absorbent's surface area must be considered when capturing methane.
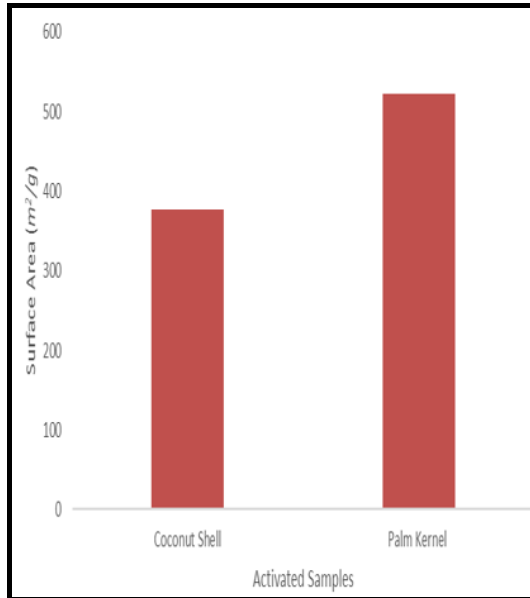

Figure 2: Graph of Surface area (m^2/g) vs Activated Samples

C. Pore Volume of CSAC and PKSAC

The results for pore volume analysis of CSAC and PKSAC were presented in figure 3 and 4 respectively. The Pore Volume of Activated Coconut Shell (CSAC) and Activated Palm Kernel Shell (PKSAC): A According to Figures 2 and 3, the pore volume of activated palm kernel shell is 0.472 cc/g, whereas that of activated coconut shell is 0.342 cc/g. This means that the pore volume of activated palm kernel shell was greater than that of activated coconut shell.

The study showed that the porosity of coconut shell activated carbon (CSAC) was 0.31 and that of palm kernel shell activated carbon (PKSAC) was

0.49 [15], corroborated this conclusion. The various raw materials used may have caused variations in the porosities of the activated carbons that were formed. Further evidence for the larger pore volume of activated palm kernel shell relative to activated coconut shell comes from a study conducted in 2010 by Lim et al., which found that the pore volume of activated palm kernel shell was 0.903 cc/g. These results were consistent with those obtained by Gao et al. (2022). PKSAC performed better than the (CSAC) sample, as indicated by the cumulative pore volume of both samples (Figure 4). This pattern is consistent with the findings of the research conducted, which showed that the number of closed pores increased in the high-, medium-, and low-rank coal samples after the clean fracturing fluid treatment. While the micropore volume rose by 0.0009, 0.00143, and 0.0035 ml/g, respectively, the specific surface area increased by 4.87, 9.06, and 57.60% [16].

Following treatment with clean fracturing fluid, the coal samples' adsorption capacity increased, which is correlated with increases in the coal sample's micropore volume, micropore percentage, and specific surface area [16]. It was clear that a treated coal sample performed well as an absorbent due to increases in micropore volume, surface area, and micropore proportion.
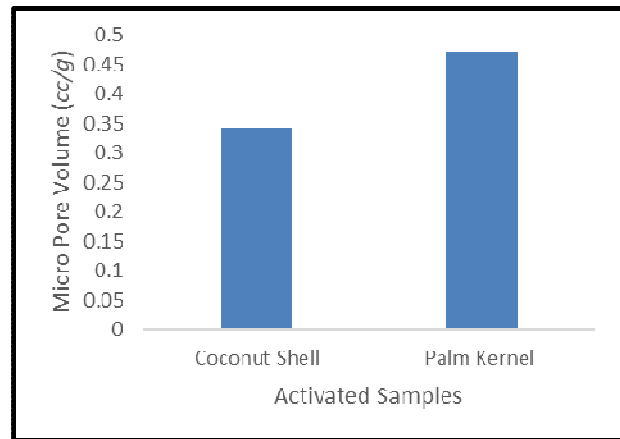

Figure 3: Graph of Micro Pore Volume (cc/g) vs Activated Samples

D. Micropore Analysis Results of Diameter and Volume of CSAC and PKSAC

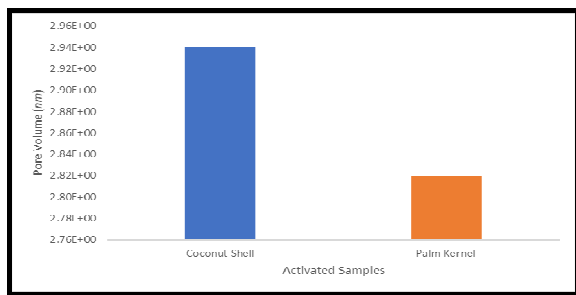The comparison between the diameter and volume of CSAC and PKSAC were shown in figure 3.

Figure 4: Compared the micro pore volume of the two activated samples (CSAC and PKSAC)

E. *Cumulative pore volumes and Surface Areas of CSAC and PSKAC*

Figures 5 and 6 showed the cumulative pore volumes and surface area of CSAC and PSKAC, comparing their performance.
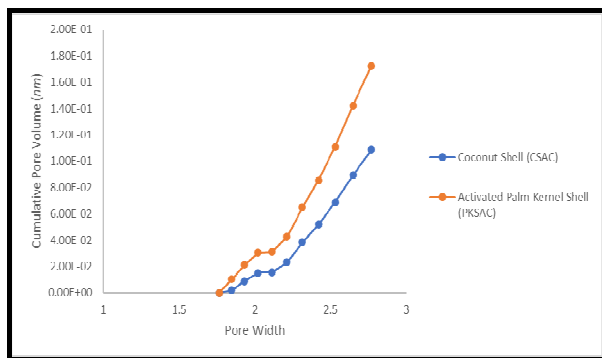

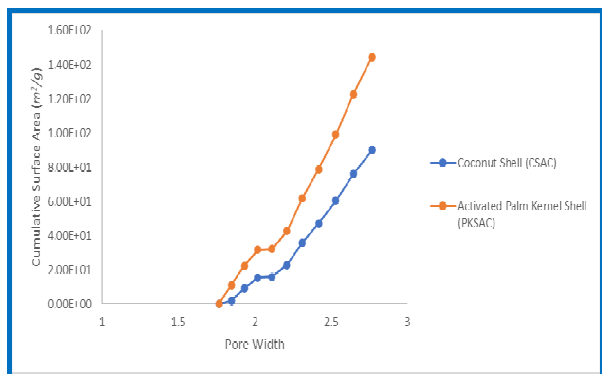Figure 5: Graph of Cumulative Pore Volume (nm) vs Pore Width of different Activated Samples more.

Figure 6: Graph of Cumulative Surface Area (m^2/g) vs Pore Width of different Activated Sample.

IV.   CONCLUSIONS

The adsorption of carbon dioxide in coconut and palm kernel shells was studied. volume and surface values of coconut shell were compared to values obtained using palm kernel shell. From the results and analysis, the conclusions were as follows:

i). It was found that PKSAC had a surface area of 521.864 m^2/g, whereas CSAC had a surface area of 377.332 m^2/g. This suggests that PKSAC was more appropriate for adsorption because higher surface area corresponds to more interactions with the gas or chemical to be adsorbed. The moisture contents of CSAC and PKSAC were found to be 2.1% and 2.4% respectively, clearly indicating that both samples close range moisture contents and could be used for adsorption processes.

ii). It was discovered that PKSAC's pore volume was larger than CSAC's. Still, the difference was not insignificant.

iii). The activation of the PKSAC and CSAC increased the surface area, volume, and proportion of micropores; as a result, these parameters were in charge of the samples' effective adsorption.

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