Synthesizes of Activated Carbon as Promising Electrode Materials for Supercapacitor Applications

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Abstract

The Preparation of sustainable and highly efficient biochars as electrodes materials remains a challenge for developing green energy storage devices. In this study, proficient carbon electrodes were produced from activated carbon (AC) derived from agricultural wastes (corncob, groundnut shells and rice husk) for supercapacitor (SC) cell via a physio-chemical technique. Biochars activated by potassium hydroxide (KOH) were explored as a prototype to be used for the preparation of electrodes for supercapacitor. The physical and chemical properties of the produced ACs were characterized using TGA, XRD, SEM and BET. The electrochemical performances of the constructed AC electrodes were studied using Electrochemical Impedance Spectroscopy (EIS). Thermal decomposition behavior TGA confirmed a suitable temperature of about 350^0C for the carbonization of the agricultural waste precursors, the structural analyses using XRD confirmed the successful transformation of the carbon-containing waste into an amorphous and carbonaceous material. The BET analysis shows that surface area for the agricultural waste derived AC samples were 514.113, 950.046 and 1088.124 m2/g for corncobs, groundnut shells and rice husk respectively. The AC derived from rice husk have the largest developed micropore content as confirmed by SEM and BET, demonstrating its suitability for applications that requires high surface area materials than the corncob and groundnut shell ACs. The electrochemical performance of the electrodes was anlysed using EIS, the Nyquist Impedance plot shows that the rice husk AC electrode sample was the closest to vertical which indicates that it has the least parallel leakage reaction, followed by the corncob and ground nut shell AC samples respectively. These results suggested that agricultural waste derived ACs are promising candidates for high-performance supercapacitors. In these studies, the rice husk was considered a higher-efficiency precursor, followed by corncob and groundnut shell for bio-based electrode preparation to be employed in SCs.

Keywords: Electrode materials, supercapacitors, Activated carbons, Agricultural waste, porous structure

1. Introduction

Biomass activated carbons (AC) are derived from various renewable organic sources such as wood, agricultural remains, and other biomass materials. They are produced through a process of carbonization and activation, resulting in a porous material with a large surface area and high adsorption capacity (Marsh & Rodríguez-Reinoso, 2006). Biomass AC have gained attention due to their sustainable nature and potential for utilization of waste materials. They find applications in environmental remediation (Jha *et al.,* 2021), water and air purification (Jjagwe *et al.,* 2021), energy storage (Zhan *et al.,* 2021), and as catalyst supports (Akbayrak *et al.,* 2020).

Biomass AC has garnered significant attention as a promising electrode material for SCs due to their unique properties, including high surface area, tunable pore structure, and excellent electrical conductivity. As an electrode material in SCs, AC offers the potential for high energy storage capacity and rapid charge-discharge cycles, making it a key component in the development of efficient energy storage devices (Dubey *et al.,* 2020). The extensive surface area and porous structure of activated carbons provide ample sites for the adsorption of electrolyte ions, facilitating the electrochemical double-layer capacitance and enhancing the overall capacitance of the supercapacitor. Furthermore, the high electrical conductivity of activated carbons enables efficient electron transport, contributing to the superior performance of SC devices (Manasa *et al.,* 2022). The utilization of biomass-derived activated carbons not only addresses the need for sustainable electrode materials but also contributes to the development of environmentally friendly energy storage technologies. As a result, research into the application of biomass activated carbons as AC electrode materials has gained significant interest in the field of energy storage and electrochemical devices (Ghosh *et al.,* 2019).

Recently, many research efforts have been done in this area to improve the performance of energy storage devices, such as supercapacitors and energy production systems such as fuel cells. However fossil fuels do not meet this demand as they are not renewable in nature (Dubey *et al.,* 2020). Hence, the utilization of bio-waste as precursor in the production of AC for use as electrode material in SC can fulfil the demand because of their low-cost accessibility. In this study, the utilization of carbon material from agricultural waste (rice husk, corncob and ground nut shell) as a potential candidate in the production of activated carbon electrodes for supercapacitor application as storage device was reported. The abundant availability, low priced and easily to be activated properties of agricultural waste-based carbon are good reasons that can be relied upon for utilization as electrode materials.

2. Review of Related Studies
In Carbon materials are commonly utilized in supercapacitors due to their distinct blend of chemical and physical characteristics, such as high conductivity, a large surface area, excellent corrosion resistance, stability at high temperatures, controlled pore structure, ease of processing, compatibility in composite materials, and relatively low cost (Pastor-

Villegasa *et al.*, 2006). Various forms of carbon materials serve as electrodes for energy storage, including activated carbons, carbon aerogels, carbon fibers, and carbon nanotubes. The process of enhancing the surface area (porosity) of carbon-based materials through thermal or chemical treatments is known as 'activation,' resulting in a diverse group of materials known as activated carbons. Due to its cost-effectiveness and higher surface area compared to other carbon materials, activated carbon is extensively employed as an electrode material in electric double-layer capacitors (EDLCs) (Zhan et al., 2021). It utilizes a complex porous structure composed of micropores (diameter < 2 nm), mesopores (diameter from 2-50 nm), and macropores (diameter> 50 nm) to achieve their high surface area. Usually, the capacitance values of activated carbons range from 100 to 200 Fg^{-1} in aqueous medium, and from 50 to 150 Fg^{-1} in organic medium. Its refined porous structure comprises of micropores (diameter < 2 nm), mesopores (diameter ranging from 2-50 nm), and macropores (diameter > 50 nm) are used to achieve a substantial surface area. Typically, the capacitance values of activated carbons range from 100 to 200 Fg^{-1} in aqueous mediums and from 50 to 150 Fg^{-1} in organic mediums. While capacitance is directly linked to surface area, empirical observations indicate that not all of the extensive surface area contributes to the device's capacitance. Larger electrolyte ions are unable to diffuse into smaller micropores, thereby hindering certain pores from participating in charge storage (Pastor-Villegasa et al., 2006). The influence of capacitance on pore size distribution of activated carbon electrodes is a major area of research in the design of EDLCs.

Conventional capacitors consist of two conducting electrodes separated by an insulating dielectric material. When a voltage is applied to a capacitor, opposite charges accumulate on the surfaces of each electrode. The charges are kept separate by the dielectric, thus producing an electric field that allows the capacitor to store energy (Kandalkar et al., 2008). For a conventional capacitor, capacitance C, is directly proportional to the surface area A, of each electrode and inversely proportional to the distance D, between the electrodes as expressed in Equation 1:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{D} \tag{1}$$

where, ε_0 is the dielectric constant (or permittivity) of free space and ε_r is the dielectric constant of the insulating material between the electrodes (Hapler & Ellenbogen, 2006). In energy storage, electric energy is stored within an electrochemical double layer (Helmholtz Layer) that forms at the interface of the electrode and electrolyte. Positive and negative ionic charges present in the electrolyte gather at the solid electrode's surface to balance out the electronic charge at the electrode surface. The thickness of the double layer is influenced by the electrolyte concentration and the size of ions, typically ranging from 5 to 10 angstroms for concentrated electrolytes (Nam & Kim, 2002). The key characteristics of any energy storage device include its energy density and power density. Energy density refers to the amount of energy that can be stored, while power density indicates how rapidly the stored energy can be delivered. The maximum stored energy E and maximum power P usable for a capacitor are determined by:

$$E = \frac{CV^2}{2} \qquad (2)$$

$$P = \frac{V^2}{4R} \qquad (3)$$

where, V is the voltage, C is the capacitance and R is the equivalent series resistance (ESR) (Katz & Carlen, 2000). An ideal energy storage system must have a high energy and power density and from the above equation it should have high capacitance, large voltage window and low ESR (Katz & Carlen, 2000). Electrochemical capacitors currently bridge the gap between batteries and traditional solid-state and electrolytic capacitors. While they offer higher capacitances compared to conventional capacitors, electrochemical capacitors have not yet reached the energy densities of mid to high-end batteries (Hapler & Ellenbogen, 2006). In the recent years due to extensive research of new electrode materials, improved understanding of ion behavior and the design of new hybrid systems combining Faradic and capacitive electrodes have increased the performance of ESs (Frackowiak, 2007).

3. Materials and Methods

3.1 Materials

Agricultural wastes (corncob, groundnut shells and rice husk) acquired locally from the respective farms at the postharvest dumping sites were used as precursors for the production of the biomass AC. Phosphoric acid (H_3PO_4), Potassium Hydroxide (KOH), Hydrochloric acid (HCl) was of Laboratory grade. Weighing balance, filter papers, beakers, petri dishes, double distilled water were acquired for the experiment. Muffle Furnace was used for the Carbonization of Agricultural wastes. Polyvinylidene Fluoride (PVDF) were used as binder for the carbon materials, pairs of Aluminum plate (3 cm by 2 cm and 0.13 mm thick) were used as current collectors, paint brushes were also used for spreading AC on the surface of the current collectors.

3.2 Methods

(a) Synthesis of Activated Carbon

The Agricultural waste samples were washed thoroughly with distilled water to remove soil and dirt, then dried at $80\,^{\circ}C$ (in an oven) to remove moisture. 100 g of dried Agricultural waste samples were weighed and then subjected to physical activation in an electric furnace, at different carbonation time ranging from 20 min, 30 min, 40 min, 50 min and 1 hour at a temperature of 300 °C. The samples obtained were weighed after physical activation and soaked in Phosphoric acid for 24 hrs followed by weighing the samples again in order to know the impregnation of Phosphoric acid in the samples and was followed by activation in muffle furnace at temperature 200 ºC for 2 hr. The carbonised material was then washed with double distilled water to remove the free alkali and dried at $100 \pm 5\,^{\circ}C$ for 2 hrs. The AC was examined using Brunauer-Emmett-Teller

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(BET), Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD). The obtained finer powders were then used for the fabrication of the cell electrode.

(b) Fabrication of Electrodes
Activated Carbon (AC) powder was soaked into KOH solution for about 24 hours. While the electrolyte solution and the AC was coated on one side of the Aluminum plate which serves as current collectors. The coated Aluminum plate was then dried at a temperature of 65 $°C$ for 5 minutes. The same process was subsequently repeated on the other pair of the Aluminum plate. Finally, the electrode was dried and ready for the fabrication of SC cells.

(c) Construction of Supercapacitors
The SC cells were constructed with KOH electrolyte-impregnated with double layered filter paper as separator and sandwiched between two prepared symmetrical AC electrodes. The electrodes were rinsed with sulphuric acid (H_2SO_4) before used. The AC electrodes were assembled, after which the cell was sealed using a sealing machine. Capacitive performances were evaluated using galvanostatic charge/discharge cycling (GCD), and electrochemical impedance spectroscopy (EIS). The tests were carried out for the two electrodes system of symmetric super-capacitors.

4. Results and Discussion

4.1 Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) Analyses
Devolatilisation of biomass materials are usually referred to in terms of three main components namely lignin, cellulose and hemicelluloses. The pyrolysis of biomass compounds by thermogravimetry analysis revealed that thermal decomposition of the precursor biomass by TGA proceeds in three stages, viz: water evaporation, active and passive pyrolysis. The mass loss TG and derivative curves DTG for rice husk are represented as a function of temperature shown in Figure 1. The reason for carrying out the TG and DTG analyses in this study was to determine the optimum temperature required for the carbonisation of the biomasses. An initial weight loss of about 4% was observed for the rice husk samples which corresponds to the loss of water and light volatile in the analysed samples from around temperature of 30 °C to 200 °C at 10 °Cmin^{-1} heating rate. The second phase with the highest weight loss (*ca.* 60%) during the pyrolysis which was seen from a temperature range of around 320 °C to 550 °C, this phase was characterized as the phase of active pyrolysis which was owed to high weight loss that may possibly be the major loss (decomposition) of cellulose and hemicellulose contents and partial loss of the lignin component of the rice husk sample. The continuous and slow weight loss, in the third stage, ranging from about 400 °C to 900 °C was due to the thermal degradation of lignin or complex high-molecular-weight components of the biomass sample. This phase was assigned to the passive pyrolysis region.

Thermal decomposition behavior (TG curve) confirmed that 350 °C was the suitable temperature to be used for the carbonization process of the agricultural waste precursors used in this study.
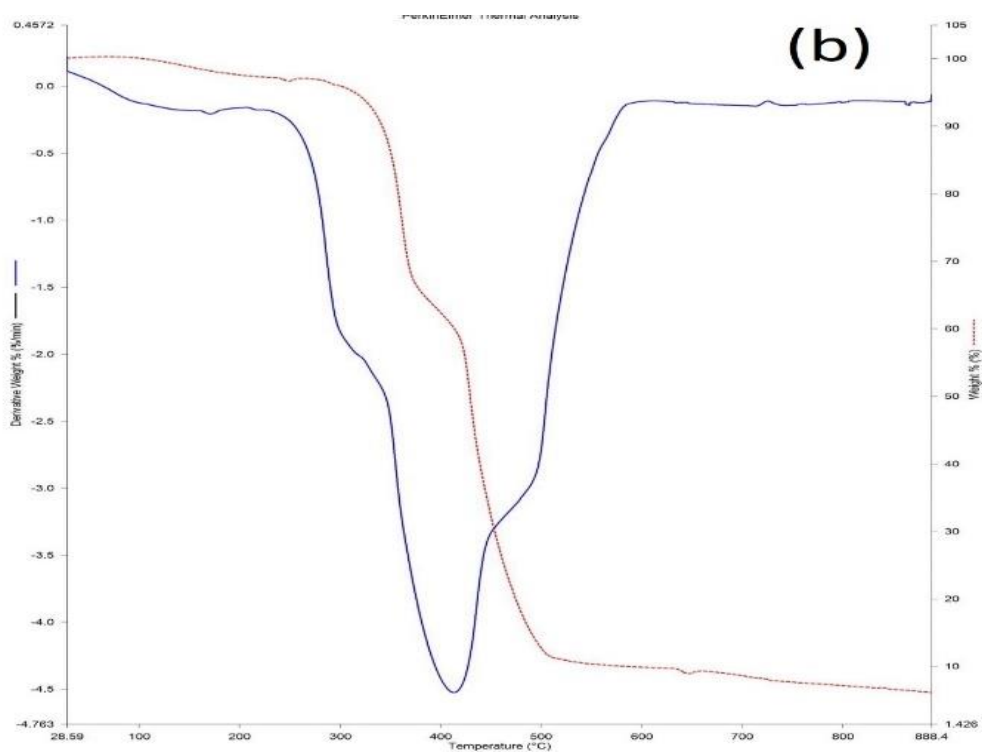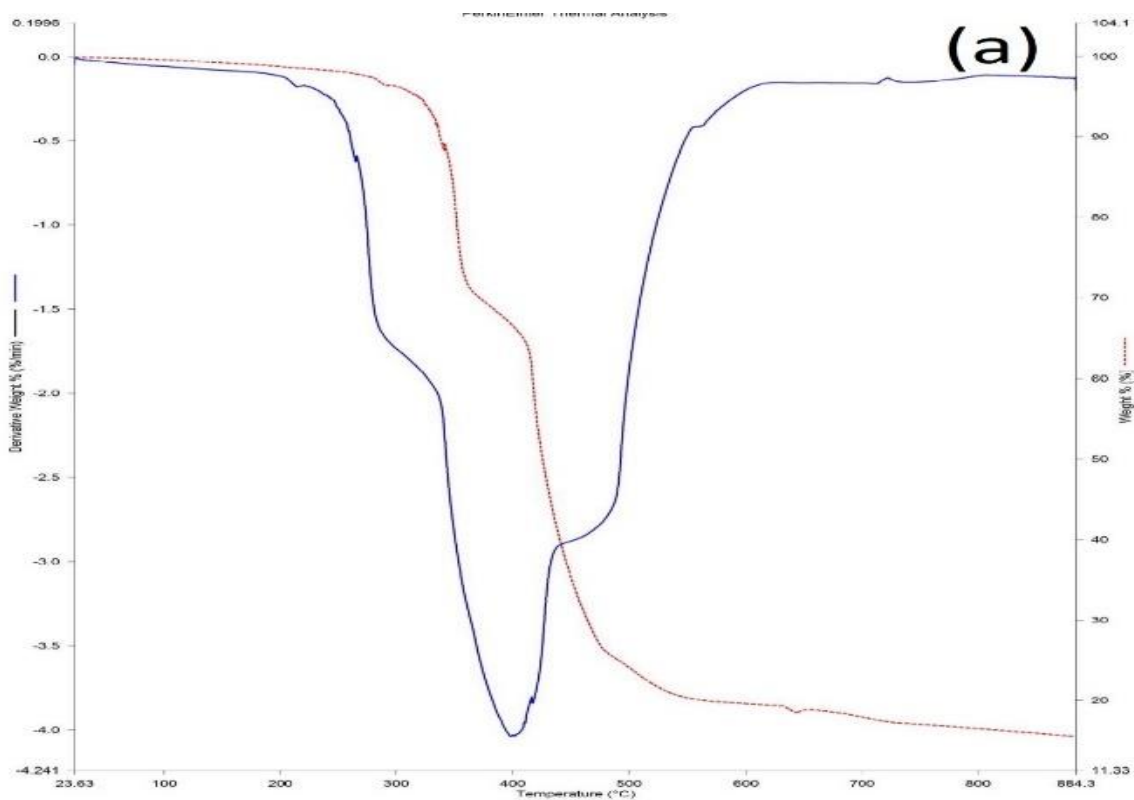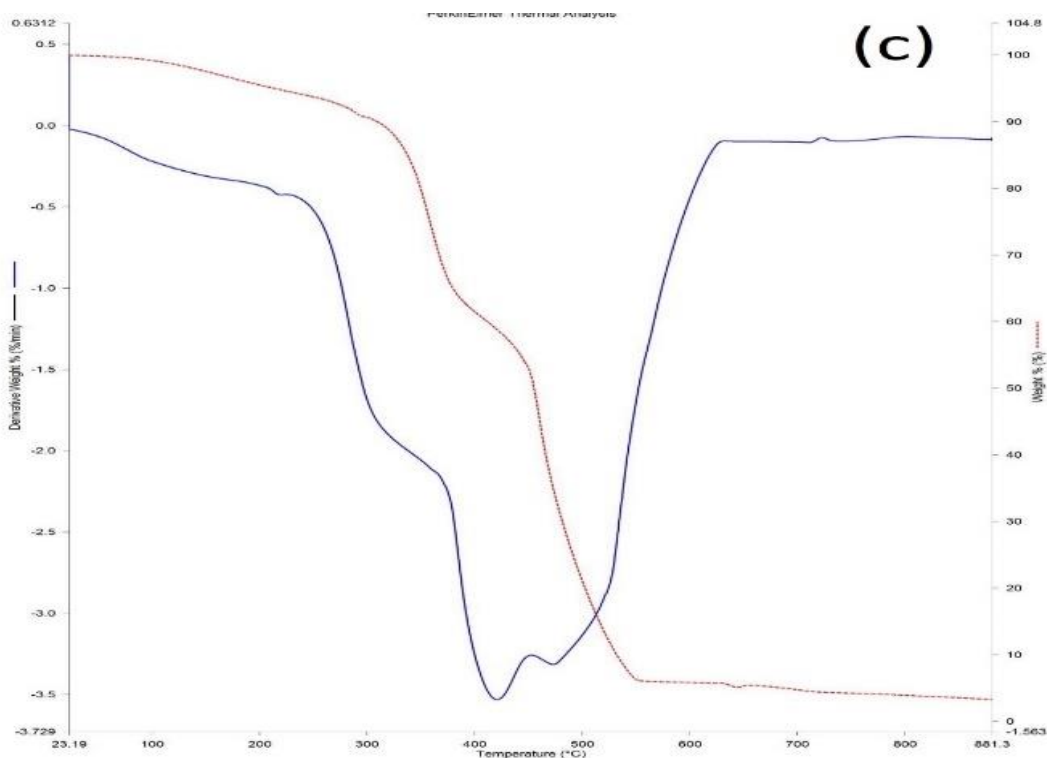
Figure 1: TGA (red line) and DTG plot (blue line) of (a) corncob, (b) groundnut shells and (c) rice husk in a nitrogen atmosphere at the heating rate of 10 °Cmin⁻¹

4.2   **X-Ray Diffraction (XRD) analysis of activated carbon samples**

The XRD pattern of corncob, groundnut shells and rice husk activated carbons at different temperatures are shown in Figure 2. (a), (b) and (c) respectively. A predominantly amorphous structure was exposed by the appearance of broad diffraction background and the absence of sharp peaks, thus, explained its crystalline carbonaceous structure. All patterns exhibit broad peaks in the range of 20° to 30° along 2θ axis which indicates the existence of amorphous silica. The two broad peaks present at 2θ axis between 20° – 30º and 40° – 50° respectively are related to the existence of more amorphous carbon which belongs to the biomass-based carbon peaks (Tan *et al.,* 2021). Nonetheless, some other peaks were still observed, which could be linked to reagents that were present due to incomplete removal during cleaning processes.
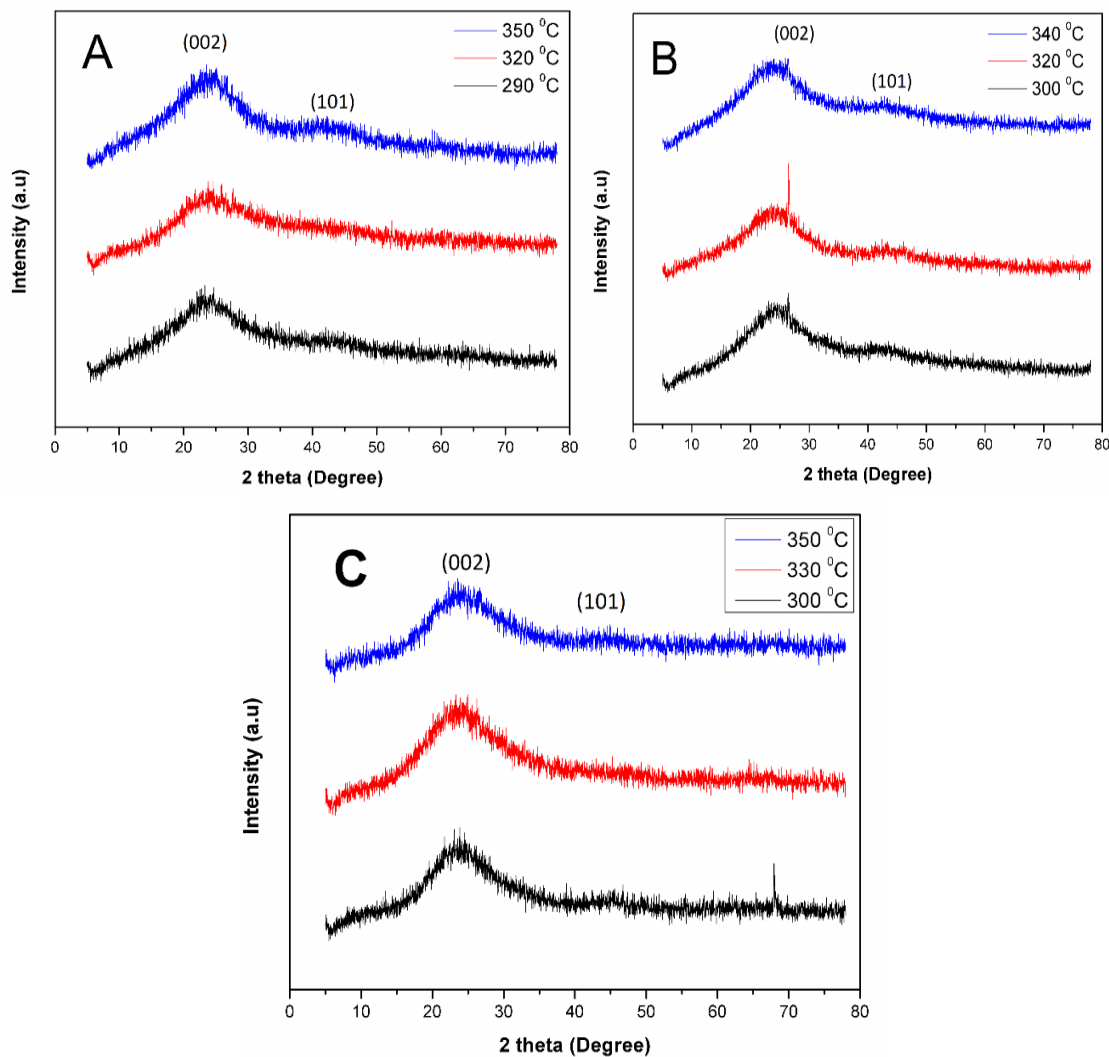
Figure 2: The XRD pattern of (a) corncob (b) groundnut shells and (c) rice husk activated carbons

4.3 **Scanning Electron Microscopy (SEM) Analysis**

The SEM images reveal details about the surface texture and topography of the prepared carbon samples. Figure 3 (a), (b) and (c) show the surface topography of corncobs, ground nut shells and rice husk activated carbons respectively, having some visible pores. Well-developed porous surface of AC was observed from the SEM micrograph as shown in Figure 3 (a), (b) and (c) which are considered as channels to the micro porous network. It showed that the AC samples have rough texture with heterogeneous surface and a variety of randomly distributed pore sizes.
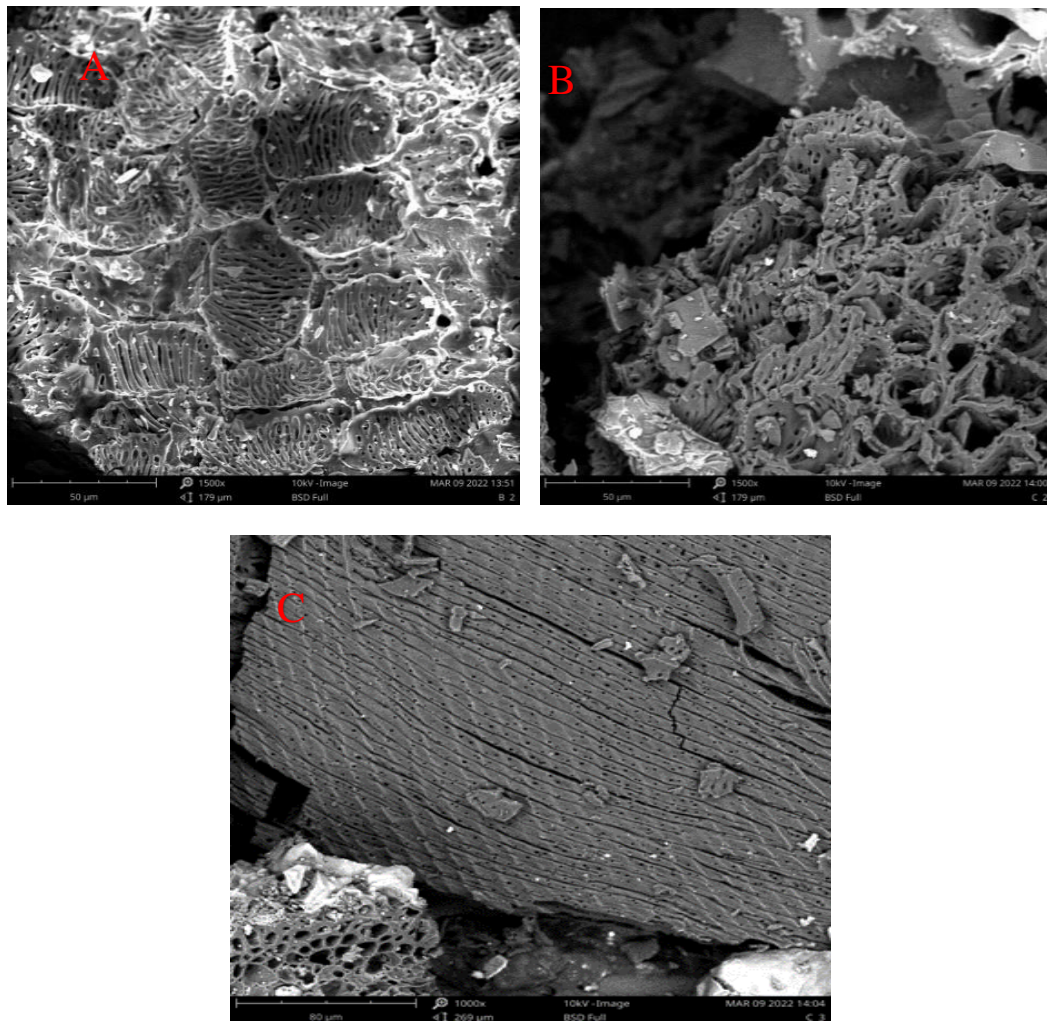
Figure 3: SEM Images of (a) corncob (b) groundnut shells and (c) rice husk activated carbons

The porous structure in all the samples were formed because most of the activation process in accordance with the presence of Phosphoric acid and the high temperature could have mainly been responsible for this. The creation of pores increases both the surface area and the pore volume and affects the efficiency of the applications of the ACs. In addition, it is easy for the activator to enter the pore interior during activation, making it form developed micro porous structures. Porosity is usually created during the removal of the volatile from the organic biomasses and creates a diverse arrangement (Dutta *et al.,* 2014).

4.4   Brunauer-Emmett-Teller (BET) Analysis

The structural properties of the corncobs, ground nut shells and rice husk activated carbon samples calculated from N_2 adsorption isotherms for BET are presented in Table 1. The surface area for the corncobs, ground nut shells and rice husk activated carbon samples are 514.113, 950.046 and 1088.124 m^2/g respectively. This indicates the presence of mesopores and a well-developed high surface area in the activated carbon sample structures which can enhance its adsorption capacity (Zhang *et al.,* 2020). In

addition, Table 1 lists all values of the micropore volumes in units of cc/g as calculated by the DFT and DA techniques. The mesopores are dominant for all the activated carbons samples. The proportion of micropores was significantly higher in rice husk activated carbon followed by groundnut shell, then corncob activated carbon. The activated carbons derived from rice husk have the largest developed micropore content, demonstrating excellent adsorption characteristics (Alam *et al.,* 2020) and its suitability for applications that require high surface area materials than the corncob and groundnut shell activated carbon. Such porosity in supercapacitor electrodes materials plays a crucial role in reinforcing the electric double-layer formation, where the pores can be accessible to electrolyte ions (Alam *et al.,* 2020).

Table 1: Structural properties of the activated carbon calculated from N2 adsorption isotherms for rice husk Activated Carbons

	Activated Carbons Samples		
	Corncob	**Groundnut shells**	**Rice husk**
BET Specific Surface Area	514.113 m²/g	950.046 m²/g	1088.124 m²/g
DFT method summary:			
Pore volume	0.174 cc/g	0.244 cc/g	0.299 cc/g
Surface area	148.831 m²/g	201.565 m²/g	411.824 m²/g
Lower confidence limit	1.766 nm	1.766 nm	1.205 nm
Fitting error	2.360%	3.476%	1.860%
Pore width (mode)	2.647 nm	2.647 nm	2.858 nm
DA method summary:			
Best E	0.815 KJ/mol	0.663 KJ/mol	5.815 KJ/mol
Best n	1.000	1.000	1.000
DA Micropore Volume	0.463 cc/g	0.838 cc/g	0.863 cc/g
Pore Diameter (mode)	2.800e + 00 nm	3.000e + 00 nm	3.100e + 00 nm

4.5 Electrochemical Impedance Spectroscopy (EIS)

Figure 4 shows the Nyquist plots of the AC electrodes from corncobs, ground nut shells and rice husk AC samples. The equivalent series resistance (ESR) values were taken at the intercept of Z' axis (real part of the impedance) and the impedance curves are slightly tilted vertical lines showing diffusion and charge transfer resistance of the electrodes. The slightly tilted vertical lines of the different biomass sourced electrode materials indicate a deviation from pure capacitive behavior (Momodu *et al.,* 2017) where the imaginary

impedance remains constant as the real impedance increases. This diffusion impedance in medium frequency indicates the efficiency of ion transfer in the interface of electrode and electrolyte (Tatara *et al.,* 2019). The plot of the rice husk AC electrode sample was the closest to vertical which suggests a low diffusion resistance of ions within the structure of the material and thus indicates that, it has the least parallel leakage reaction (Okafor, 2016), followed by the corncob and ground nut shell derived samples respectively, which is in accordance with the porous characteristic of the ACs as indicated by the SEM and BET analyses. It can be deduced that the more developed microporous structured ACs facilitates the capacitance performance of the fabricated AC electrodes.
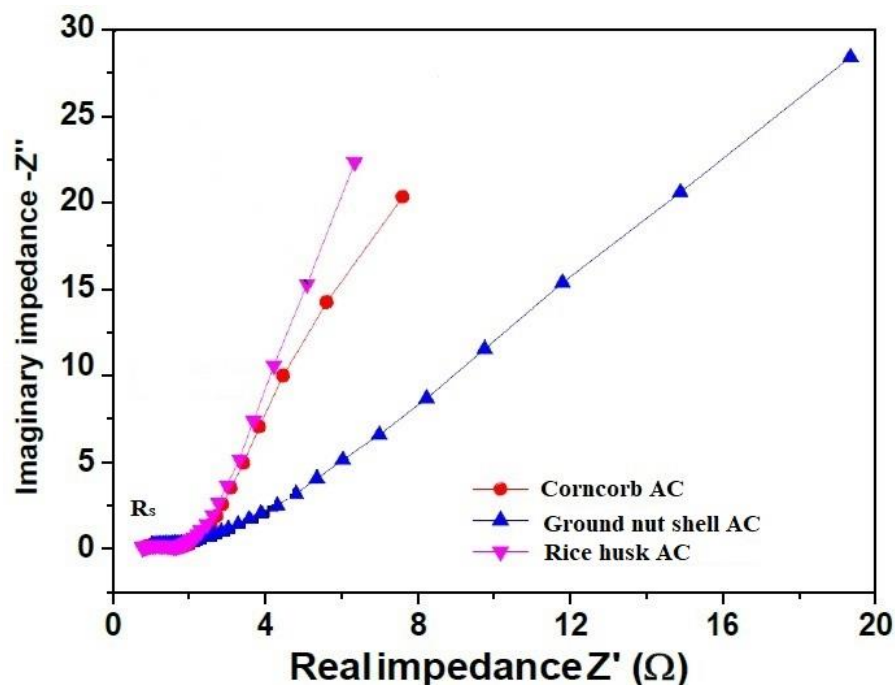
Figure 4: The Electrochemical Impedance Spectroscopy (Nyquist Impedance) plot of corncob, groundnut shells and rice husk derived AC samples

5. Conclusion

The activated carbon from agricultural wastes of rice husk, corncob and ground nut shell was successfully synthesized via carbonization and activation processes. The SEM of these materials as well as the gas adsorption analysis measurement (BET) results showed good porosity and surface area properties of the chosen waste plant biomass materials. The BET analysis shows that surface area for the agricultural waste derived AC samples are 514.113, 950.046 and 1088.124 m2/g for corncobs, ground nut shells and rice husk respectively. Thus, all the materials under study have shown potential in applications as supercapacitor electrode materials. The XRD result confirmed the successful transformation of the carbon-containing waste into an amorphous and carbonaceous material. The AC derived from rice husk have the largest developed micropore content as confirmed by SEM and BET, demonstrating its suitability for applications that requires high surface area materials than the corncob and groundnut shell ACs. Electrochemical

performances of the different biomass derived carbon materials have also shown strong correlation between capacitance performance and morphology of the prepared ACs. The electrochemical performance of the electrodes was analyzed using EIS. Nyquist Impedance plot shows that the rice husk AC electrode sample was the closest to vertical which indicates it has the least parallel leakage reaction, followed by the corncob and ground nut shell AC samples respectively. These results suggested that agricultural waste derived ACs are promising candidates for high-performance supercapacitors. The findings of this study show that the rice husk is considered a higher-efficiency precursor, followed by corncob and ground nut shell for bio-based electrode preparation to be employed in SCs. Thus, this study has shown a valuable path towards sustainable and green energy storage solutions.

Funding

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