Original Article

Synergistic Hybrid Activation Strategy for Enhancing Electrochemical Properties of Agro-Biomass Derived Activated Carbon for Supercapacitors

Esther Chioma Udochukwu

Department of Chemical Engineering, Federal University Otuoke, Bayelsa State, Nigeria.

[1]*Corresponding Author : udochukwuec@fuotuoke.edu.ng*

Abstract - This research addresses a unique hybrid activation approach that combines physical and chemical procedures to enhance the structural and electrochemical features of activated carbon obtained from agro-biomass, notably coconut shells. Potassium hydroxide (KOH) and sodium hydroxide (NaOH) acted as activating agents, and the resulting activated carbons were meticulously analysed using advanced techniques, including scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, and X-ray diffraction (XRD). Among the samples, NaOH-activated carbon (NaOH-AC) demonstrated exceptional performance, with a carbon content of 90.11 wt%, 73% graphite, and 19% silicon, which enhances its electrical conductivity. Furthermore, NaOH-HAC exhibited a substantial specific surface area of 1315.396 m²/g, an average nanopore size of 2.103 nm, and a total pore volume of 0.632 cc/g. Electrochemical evaluations revealed exceptional performance in an aqueous electrolyte, with NaOH-HAC attaining a specific capacitance of 474.75 F/g, an energy density of 20.00 Wh/kg, and a power density of 4500 W/kg following 8000 charge-discharge cycles at a current density of 0.8 A/g and a scan rate of 5 mV/s. This work presents a sustainable, economical approach for generating high-performance supercapacitor electrodes from agro-biomass, giving considerable advances in material structure and electrochemical behaviour for energy storage applications.

Keywords - Nanostructured activated carbon, Aqueous electrolyte, Electrochemical analysis, Electrochemical capacitor, Agro-based biomass.

1. Introduction

The increased need for clean and renewable energy sources has driven tremendous interest in creating revolutionary materials for energy storage and conversion technologies [1]. Activated Carbon (AC) has become a versatile and widely used material in research thanks to its high porosity, expansive surface area, and adaptable surface chemistry.[2], [3]. Recently, attention has shifted towards synthesising and characterising nanostructured AC derived from renewable biomass resources for use in various energy storage devices, particularly supercapacitors and batteries [4]. Agro-biomass, such as wastes from agricultural activities, presents a plentiful and environmentally favourable feedstock for manufacturing nanostructured carbon material [5], [6], [7], [8]. Among the numerous agro-biomass sources, coconut shells (Cocos nucifera) have gained substantial attention due to their broad availability, cheap, and favourable carbonaceous properties [9], [10]. The conversion of coconut shells into AC produces valuable materials with promising uses in energy storage devices, including supercapacitors and batteries [8], [11], [12], [13]. The synthesis of nanostructured

ACs comprises multiple essential steps, including carbonisation, physical and chemical activation, and post-treatment operations, each of which can considerably influence the final material properties [3], [14], [15], [16], [17]. Characterisation methods such as SEM-EDX, XRD, BET, and FTIR are vital in understanding the morphological, structural, and chemical features of the synthesised materials [13], [18], [19]. Understanding the relationship between the synthesis parameters, microstructure, and electrochemical properties of nanostructured AC is critical for enhancing its performance as an electrode material in energy storage devices [2], [13], [20]. To evaluate Coconut Shell Activated Carbon (CSAC) electrodes for supercapacitors, a range of electrochemical tests is necessary, including Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD), Electrochemical Impedance Spectroscopy (EIS), and cycle stability assessments. These methodologies elucidate critical performance characteristics like specific capacitance, energy and power density, ion transport, and long-term durability. CSAC has proven to perform well in various evaluations, making it a potential and sustainable material for energy

storage applications. Continued tuning of its pore structure and surface chemistry can further increase its electrochemical characteristics. CV is one of the most extensively used techniques to evaluate the charge storage behaviour of supercapacitor materials. It includes sweeping the electrode voltage consistently and monitoring the resultant current, allowing researchers to analyse the capacitive behaviour and determine the electrode material's specific capacitance. CSAC electrodes often display rectangular CV curves, indicating optimal double-layer capacitance.

This form demonstrates effective charge storage through electrostatic interactions without large resistance losses. Recent research by [21] and [20] has demonstrated capacitive behaviour for CSAC materials in alkaline electrolytes. The specific capacitance is calculated by integrating the area beneath the CV curve. For example, [22] observed specific capacitance values between 260 and 300 F/g for CSAC depending on the activation procedure and electrolyte employed. A well-performing electrode material should preserve its rectangular CV shape at high scan rates.

Studies by [23] demonstrated that CSAC retains this form at scan rates up to 100 mV/s, demonstrating the material's high-rate capabilities and efficient ion diffusion.GCD is a fundamental technique for measuring the energy storage capacity and the realistic operating conditions of Electrochemical Capacitors (ECs). The procedure entails providing a steady current to the electrode and monitoring the voltage variation over time. Ideal capacitive materials exhibit symmetric triangular GCD curves, indicating efficient and reversible charge storage. [24] demonstrated this symmetry in CSAC electrodes, showing minimal resistance and good energy storage efficiency.

The specific capacitance derived from GCD is computed using the discharge period, potential range, and current density. For example, [13] reported a specific capacitance of 320 F/g for CSAC electrodes in a 1 M Na_2SO_4 electrolyte at a current density of 1 A/g. GCD testing at increasing current densities helps measure the rate capacity of the material. [2] CSAC retains up to 90% of its capacitance even at greater current densities, indicating outstanding performance under quick charging and discharging situations. EIS is incorporated to examine the internal resistance and ion transport characteristics of any type of material for electrodes in ECs. The procedure involves delivering an AC voltage and measuring the impedance response across a broad frequency spectrum. EIS data is commonly shown as a Nyquist plot, illustrating impedance's real and imaginary components. For CSAC, a little semicircle in the high-frequency zone reflects the charge transfer resistance, whereas a vertical line in the low-frequency region displays optimal capacitive behaviour. [25] CSAC electrodes have a narrow semicircle with low transfer resistance, suggesting high conductivity and efficient

ion transport. Cycling stability is a crucial performance indicator for supercapacitors, as it indicates the long-term endurance of the electrode material throughout successive charge-discharge cycles. This test is normally carried out over thousands of cycles and determines the capacitance retention. CSAC electrodes have shown remarkable cycling stability, with [23] showing that the material kept 95% of its original capacitance after 8,000 cycles. Such durability is related to the enduring pore structure and steady electrochemical activity of CSAC.

Power and energy densities are essential metrics for ECs since they define how much energy can be held and how rapidly it can be released. Energy density is determined using the device's specific capacitance and voltage range. [12] reported that CSAC electrodes generally display energy densities between 5 to 15 Wh/kg, depending on the electrolyte and operating circumstances. Higher energy densities are often reached with organic electrolytes or hybrid supercapacitors combining faradaic and capacitive storage processes. While power density measures the pace at which energy can be provided, it is inversely related to the ESR. [24] reported that CSAC electrodes often display power densities ranging from 400 to 800 W/kg, depending on the current density and electrolyte.

This makes them suited for high-power applications like fast charge-discharge cycles. This work intends to establish a sustainable and efficient approach to manufacture high-performance activated carbon from coconut shell biomass, utilizing a hybrid activation method that includes both physical and chemical activation techniques. The research focuses on increasing the produced carbon material's structural qualities and electrochemical performance, making it more suited for supercapacitor electrodes. A complete investigation of the material's composition, surface area, pore structure, and electrochemical behaviour is done to evaluate the effectiveness of the activation process and its potential for energy storage applications.

2. Materials and Methods
2.1. Material
The agro-biomass utilized in this study consists of coconut shells. Physical activation is achieved using steam, while KOH and NaOH serve as chemical activation agents. N-methyl pyrrolidone, nickel foam, polyvinylidene fluoride binder, and carbon black are employed for electrode fabrication. Additionally, a 1 M KOH solution is used as the aqueous electrolyte. HCl and deionized water were used to wash the alkaline-based AC.

2.2. Research Method
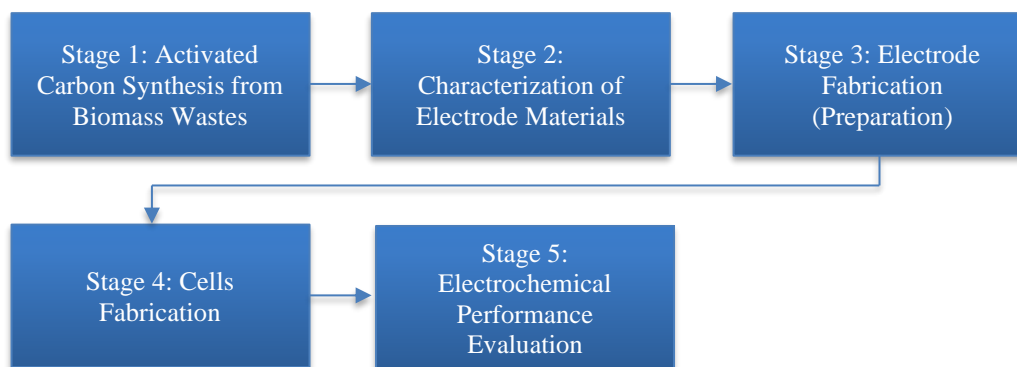The research used a well-defined stepwise procedure, as shown in Figure 1.

Fig. 1 Stepwise procedure for the fabrication of electrochemical capacitor from coconut shell

2.2.1. Hybrid Synthesis of Electrode Material

The Coconut Shell Biomass (CSB) was sourced locally as waste from the Otuoke Community Market in Bayelsa State. Initially, the biomass was crushed into smaller pieces, thoroughly washed, and then oven-dried. A quantity of 50 g of the dried material underwent initial carbonisation in a muffle furnace at 500 °C for 5 hours, with a controlled heating rate of 5 °C/min. The resulting Calcinated CSB (CCSB) was then ground into a fine powder using a crucible and sieved through a 100 μm electric sieve to achieve uniform particle size. Physical activation was conducted using the calcinated, sieved CCSB, which was steamed in a water bath for 6 hours before chemical activation. For the chemical activation, two containers were prepared, one containing 15 ml of a 2 M KOH solution and the other with 15 ml of a 2 M NaOH solution, each mixed with 10 g of CCSB. The samples were impregnated for 24 hours and subsequently underwent a second carbonisation in a muffle furnace at 600 °C. Following the chemical and thermal activation processes, each sample was washed with 5 ml of Hydrochloric Acid (HCl) and thoroughly rinsed with deionized water until neutral, achieving a pH of 7. Finally, the KOH Hybrid Activated Carbon (KOH-HAC) and NaOH Hybrid Activated Carbon (NaOH-HAC) were dried in an oven at 90 °C for 24 hours.

2.2.2. Characterization of Electrode Material

Various analytical techniques are utilised to evaluate the structural and morphological characterisation of KOH-HAC and NaOH-HAC. These techniques include:

Surface Area Analysis

Surface area and pore size distribution are determined using nitrogen adsorption-desorption isotherms measured by a technique known as BET analysis. A higher surface area and well-defined pore structure indicate better electrochemical performance.

Microscopic Imaging

SEM, EDX elemental analysis, and FTIR for functional groups analysis are utilised to visualise the morphology and microstructure of the carbon material. These techniques provide insights into the surface morphology, pore structure, and particle size distribution.

Structural Analysis

XRD and Raman's spectroscopy are employed to analyse the crystallinity and structural properties of the carbon material. These techniques help understand the degree of graphitisation and the presence of functional groups on the carbon surface, which influence its electrochemical behaviour.

2.2.3. Electrodes Fabrication

The characterised HAC with better properties suitable for electrode material was used as the main material in the fabrication of electrodes. A composite containing 85 wt.% HAC, 10 wt.% polyvinylidene fluoride (PVDF), and 5 wt.% carbon black was prepared using N-methyl-2-pyrrolidone (NMP) as the solvent. Nickel foam, chosen for its porous structure, was used as the current collector. The nickel foam was coated with the slurry, dried at 70 °C for 5 hours, and then cut into circular discs for assembly into coin cells.

2.2.4. Cell Fabrication

The cell is a double-electrode configuration, and the electrolyte used is 1 M KOH. One disc of the electrode was placed on the bottom of the coin cell case, and a filter paper soaked in the electrolyte was placed on top of the electrode, while the second disc was placed on top of the separator. The cell was filled with 5 ml of the electrolyte to ensure proper wetting. The edges of the cell assembly were sealed to prevent leakage and contamination of the electrolyte.

2.2.5. Electrochemical Performance Evaluation

All electrochemical measurements were carried out using a Biologic VMP-300 Potentiostat. Evaluating electrochemical performance in supercapacitors involves measuring and analysing various parameters to determine their energy storage capacity, power density, and durability. One of the key parameters is capacitance, which quantifies the amount of electrical energy that can be stored per unit voltage. Capacitance measurements were performed using Electrochemical Impedance Spectroscopy (EIS) techniques.

Another important parameter is the specific energy, which calculates the energy stored per unit mass or volume. This was determined through charge-discharge cycling experiments, where the supercapacitor is charged to different voltages and then discharged while monitoring the energy release. The cycle life was also evaluated to assess the long-term performance and durability of the supercapacitor. This was achieved by subjecting the device to repeated charge-discharge cycles and monitoring any capacitance or energy storage capability degradation over time. The power density, which characterises the rate at which energy can be delivered or absorbed by the supercapacitor, was evaluated by measuring the charge and discharge rates.

Fig. 2 Synthesis of Bio-based activated carbon electrode material

3. Results and Discussion

3.1. Analysis of Material Morphologies, Structures, and Chemical States

3.1.1. X-ray Diffraction Analysis (XRD)

The crystalline structure of KOH-HAC and NaOH-HAC were analysed using XRD (Figures 2 & 3). The XRD pattern shows a prominent peak at $2\theta = 20.93°$ (Figure 2a), indicating the presence of carbon-based structures. The broad peak centred around $2\theta = 20\text{-}25°$ (Figures 2a & 3a) suggests amorphous carbon, which is typical for activated carbon. The intensity and width of the peaks reveal the crystallinity of the material, with higher intensity and narrower peaks indicating higher crystallinity [26]. A balance between crystallinity and porosity is crucial for supercapacitor applications, as both impact electrode performance [2]. The analysis (Figure 2b) shows that NaOH-HAC comprises 73% graphite, 4% Sulfohalite, 5% Osumilite, and 19% silicon oxide. The high graphite content (73%) implies superior electrical conductivity, necessary for effective charge transfer and quick charge/discharge cycles in supercapacitor electrodes [27].
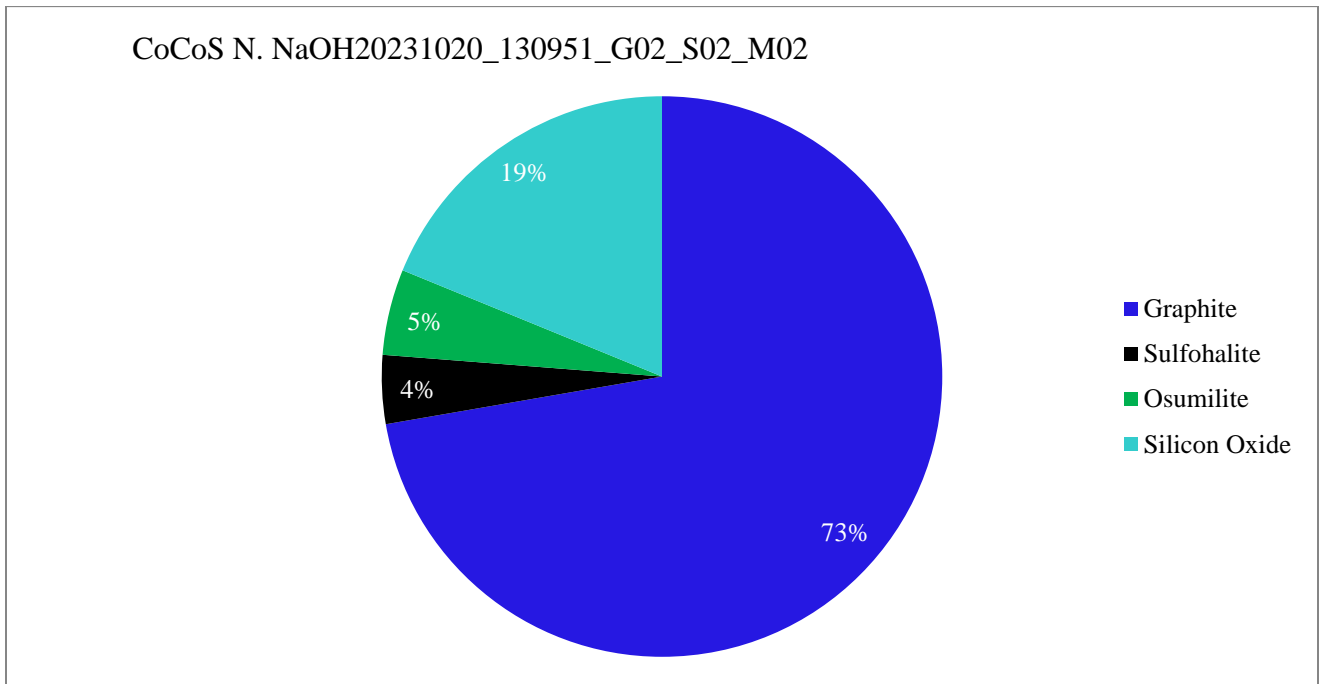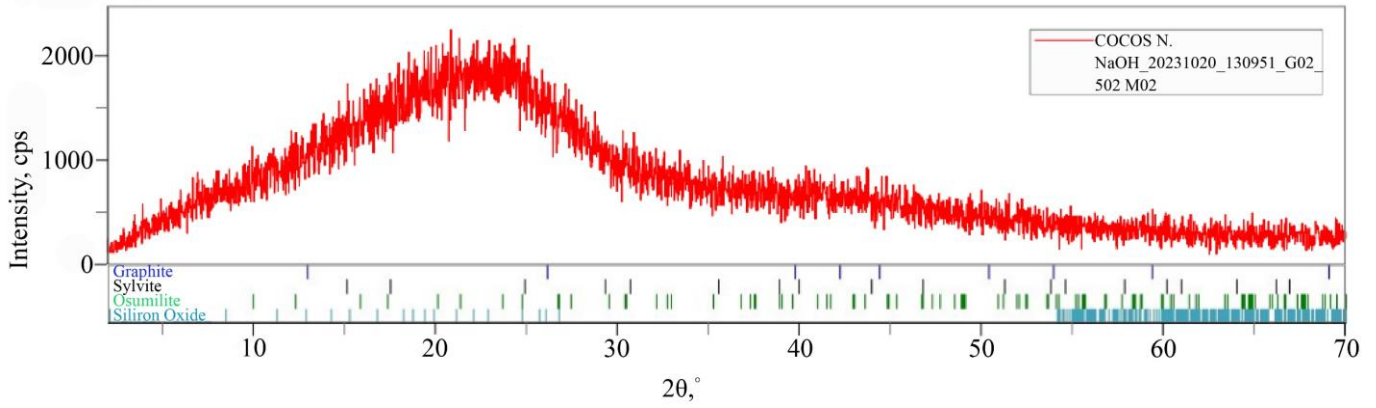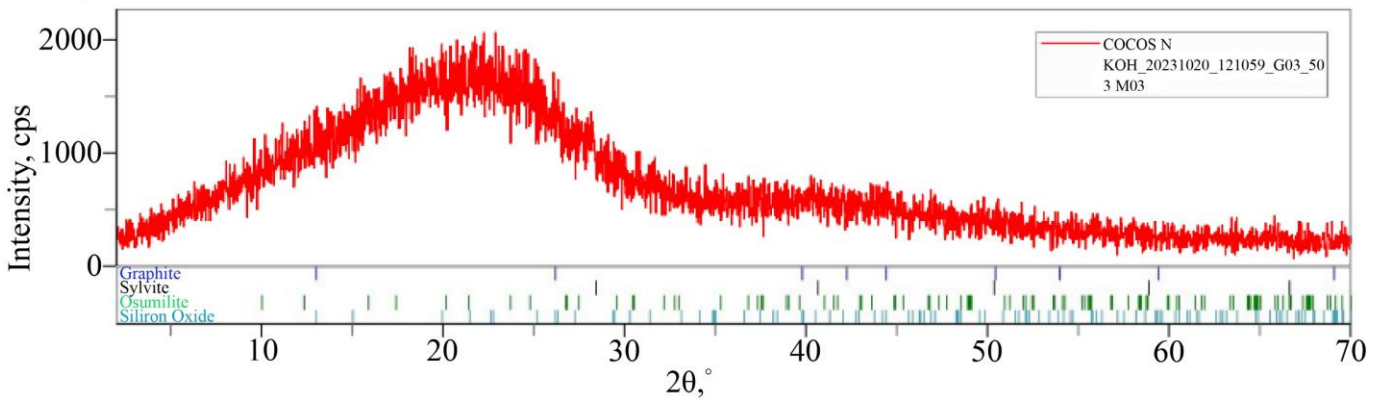
Fig. 3 X-ray Diffraction Analysis (XRD) (a & b) for NaOH-HAC

CoCoS N. KOH20231020_121059_G03_S03_M03

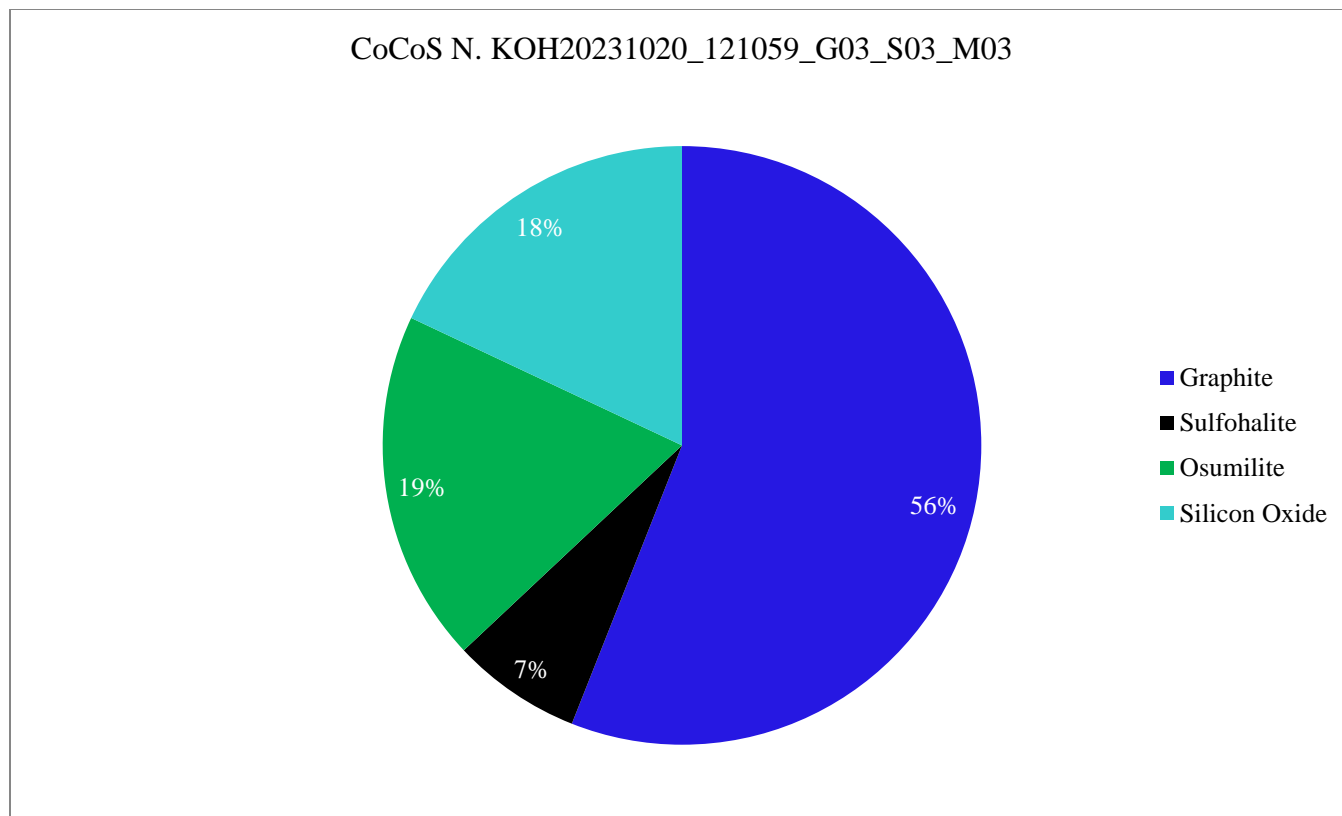- Graphite
- Sulfohalite
- Osumilite
- Silicon Oxide

Fig. 4 X-ray Diffraction Analysis (a & b) for KOH-HAC

3.1.2. Raman Spectroscopy

The Raman spectroscopy graph of coconut shell KOH-HAC, as shown in Figure 4a and sodium and NaOH-HAC in Figure 4b, provide insights into the materials' structure and composition.

Figures 4a and b show the presence of D and G bands, indicating a mix of amorphous and crystalline carbon, which is beneficial for supercapacitor applications [20]. The defects indicated by the D band can provide additional active sites for ion adsorption, while the graphitic domains indicated by the G band contribute to good electrical conductivity.

The activation process with NaOH and KOH introduced various oxygen-containing functional groups, enhancing the pseudocapacitance of the material. These functional groups are essential for increasing the overall capacitance through redox reactions. The intensity and positions of the peaks in both spectra are quite similar, suggesting that both activation processes result in comparable structural and compositional features. The slight differences in peak intensities indicate variations in the degree of disorder, graphitization, or surface functionalities introduced by the different activation agents.

3.1.3. Scanning Electron Microscope Analysis (SEM)

The SEM images of Figures 5a and 5b (1000x and 2000x Magnification) KOH-HAC show a well-developed porous structure with numerous open-cell pores. At higher magnifications, the pores appear uniformly distributed and interconnected. These features suggest a high surface area, which is beneficial for supercapacitor electrodes as it allows for more active sites for ion adsorption [28], [29].

The SEM images of Figures 5c and 5d (1000x and 2000x Magnification) NaOH-HAC show similar characteristics to the KOH-AC. The NaOH-HAC also shows a porous structure with many open-cell pores. At higher magnifications, the pores appear slightly larger but also uniformly distributed.

This structure indicates a high surface area and good porosity, which are essential for effective ion transport and charge storage. Although the pores in the KOH-HAC seem more interconnected, which might enhance ion transport within the electrode material, the NaOH-HAC shows slightly larger pores, potentially facilitating faster ion diffusion.

The high level of pore opening in both samples indicates a large surface area, which is crucial for supercapacitor performance. Larger surface areas improve the charge storage capabilities by providing more sites for electro-adsorption processes [27]. Using KOH and NaOH as activating agents has created a porous structure by dissolving organic residues and removing volatile compounds.
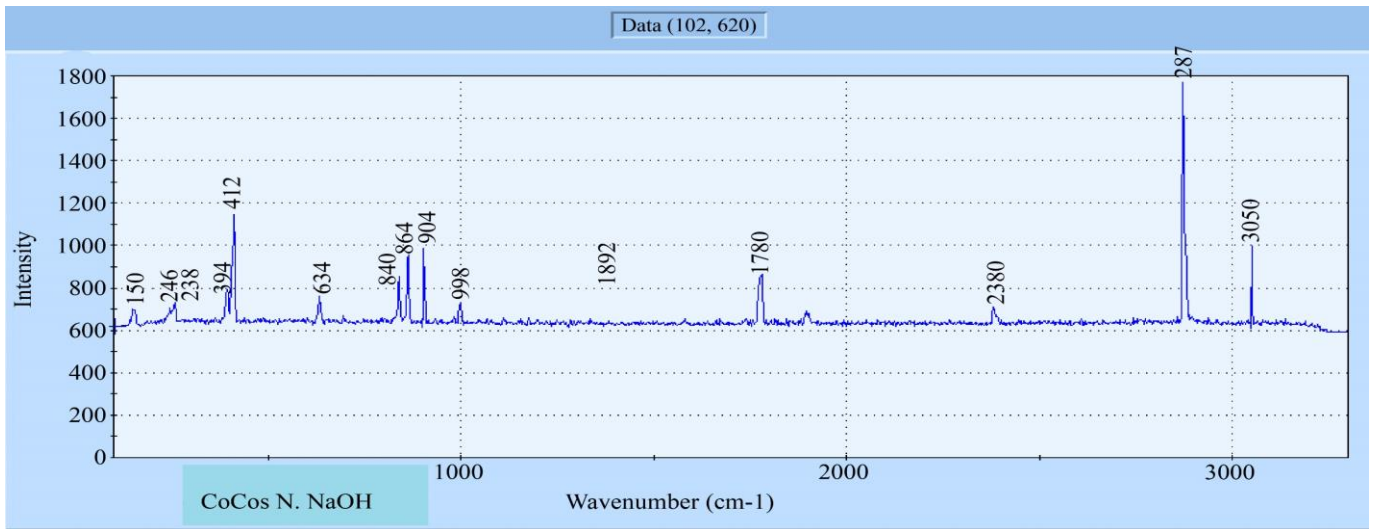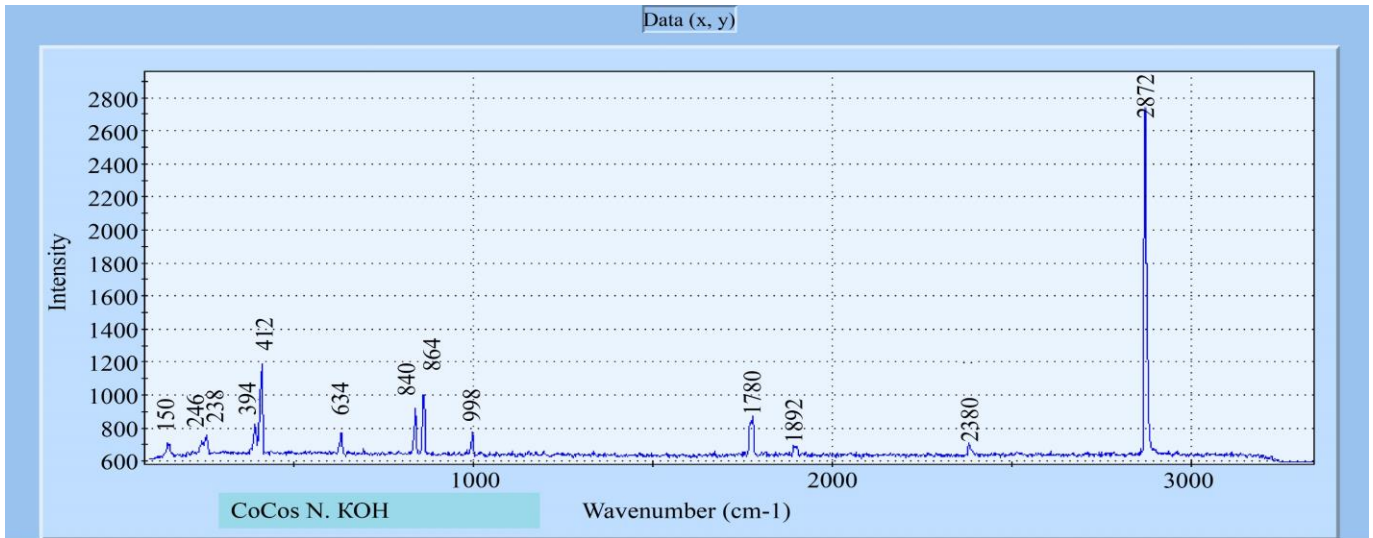
Fig. 5 Raman Spectrum for Cocos Nucifera (Coconut Shell) (a) KOH-HAC (b) NaOH-HAC
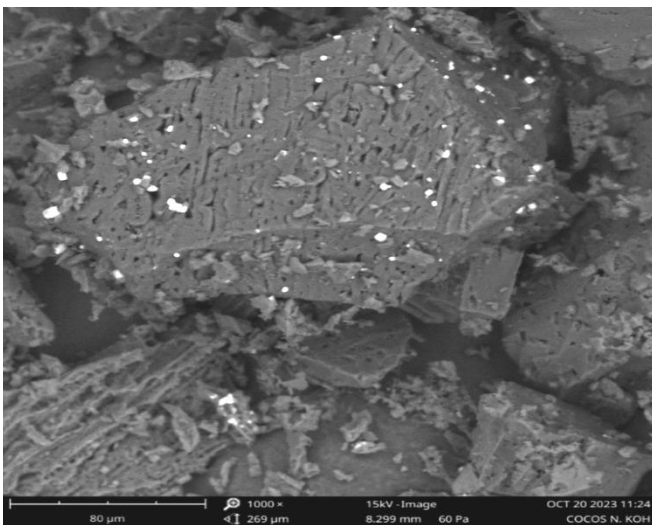

Fig. 6a SEM (KOH) 30μm 2000x magnification   **Fig. 6b SEM (KOH) 80μm 1000x magnification**
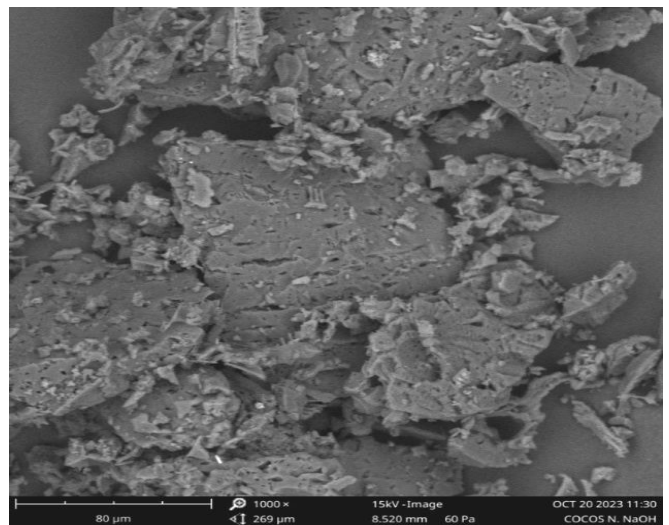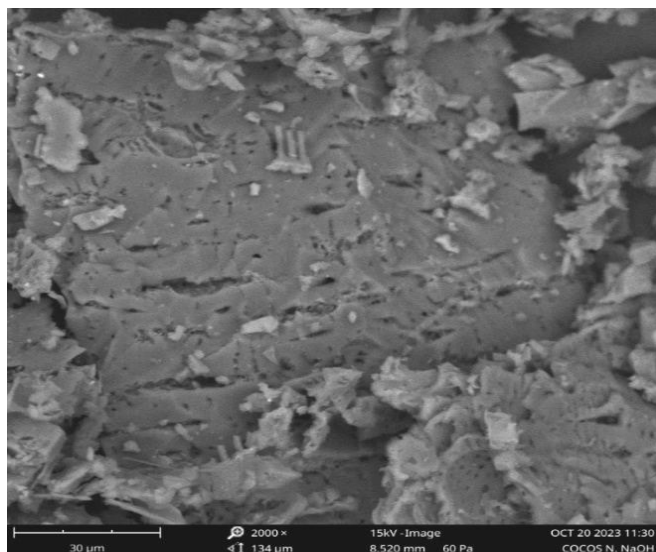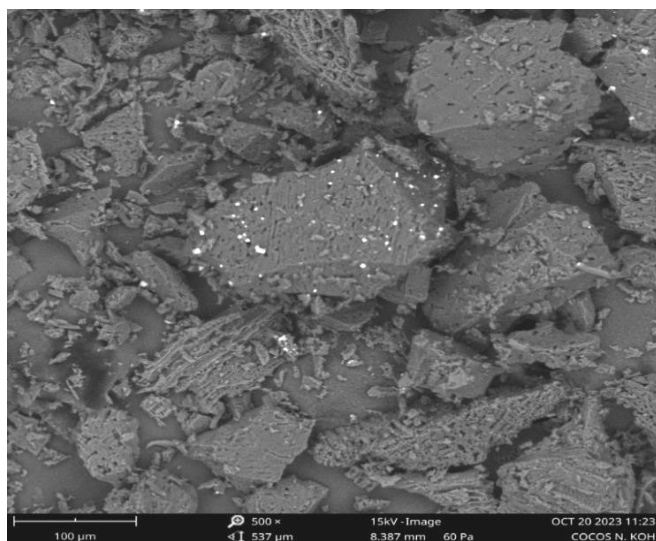
3.1.4. Energy Dispersive Spectroscopy (EDX) Elemental Analysis

The EDX microanalysis of the activated carbon samples, as shown in Tables 1a and b, provides detailed insights into their elemental compositions. The KOH-HAC contains a higher carbon content of 92.26 wt% than the NaOH-HAC of 90.11 wt%. This higher carbon content suggests that the KOH activation process is more effective in increasing the carbon proportion in the biomass material. Both activation processes significantly increase the carbon content from the pre-activation levels, indicating the effective removal of metallic and non-metallic constituents from the original lignocellulosic biomass.

3.1.5. Fourier Transform Infrared (FTIR) Analysis

Figures 6a and b present the FTIR spectra of AC derived from coconut shells (Cocos nucifera), highlighting the surface functional groups present after activation. The spectra indicate that most functional groups on the surface of the samples were removed during the carbonization or activation process. This is typical as high-temperature treatments during activation often eliminate many surface functionalities. Despite losing many functional groups due to the activation, some key functional groups were retained, such as Hydroxyl stretching (O-H) around 3347/cm and aromatic C=C stretching. The KOH-HAC peaks at approximately 1573.88/cm and 1169.21/cm. The NaOH-HAC peaks at approximately 1572.78/cm and 1167.45/cm. Comparing the KOH and NaOH-HACs, it is observed that the peak intensities for these functional groups are more pronounced in KOH-HAC compared to NaOH-HAC. This shows that the chemical composition of the precursor and the kind of activating agent considerably impact the surface chemistry of the generated activated carbon.. The presence of hydroxyl and aromatic C=C functional groups will enhance the electrochemical performance of activated carbon when used as supercapacitor electrodes.

Fig. 6c   SEM (NaOH) 30µm 2000x magnification

Fig. 6d SEM (NaOH) 80µm 1000x magnification

Table 1a. KOH-HAC Energy Dispersive Spectroscopy (EDX) elemental analysis

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	94.66	92.26
7	N	Nitrogen	4.19	4.76
17	Cl	Chlorine	0.34	0.99
19	K	Potassium	0.21	0.66
13	Al	Aluminium	0.15	0.33
12	Mg	Magnesium	0.11	0.22
11	Na	Sodium	0.11	0.20
14	Si	Silicon	0.09	0.19
15	P	Phosphorus	0.06	0.16
16	S	Sulphur	0.06	0.15
20	Ca	Calcium	0.03	0.08
22	Ti	Titanium	0.00	0.00
26	Fe	Iron	0.00	0.00

Table 1b. NaOH-HAC Energy Dispersive Spectroscopy (EDX) elemental analysis

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	93.20	90.11
7	N	Nitrogen	5.35	6.03
17	Cl	Chlorine	0.49	1.41
20	Ca	Calcium	0.18	0.59
13	Al	Aluminium	0.16	0.36
14	Si	Silicon	0.15	0.34
15	P	Phosphorus	0.09	0.24
11	Na	Sodium	0.12	0.22
12	Mg	Magnesium	0.10	0.20
16	S	Sulphur	0.08	0.20
22	Ti	Titanium	0.05	0.17
26	Fe	Iron	0.03	0.14
19	K	Potassium	0.00	0.00

Table 2. BET Comparison between KOH-HAC and NaOH-AC

Activating Agent	Surface Area (m²/g)	Pore Volume (cc/g)	Pore Diameter (nm)
NaOH	1315.396	0.632	2.103
KOH	821.787	0.401	2.110

These groups can contribute to pseudocapacitance and improve the overall capacitance of the material [30]. Based on the FTIR analysis, both KOH and NaOH-HAC retain functional groups beneficial for supercapacitor applications. However, the enhanced surface chemistry in KOH-HAC makes it a more suitable candidate for producing high-performance supercapacitor electrodes.

3.1.6. Brunauer-Emmett-Teller Analysis (BET)

From Figure 7a, NaOH-HAC shows a significantly higher surface area of 1315.396 m²/g compared to Figure 7b, KOH-HAC of 821.787 m²/g. High surface area is beneficial for supercapacitor applications [2]. NaOH-HAC also exhibits a higher pore volume of 0.632 cc/g than KOH-HAC of 0.401 cc/g. Large pore volumes enhance the material's ability to store electrolytes, thus improving the capacitance [31]. NaOH and KOH-ACs have similar pore diameters, with NaOH-HAC having a slightly smaller pore diameter of 2.103 nm than KOH-HAC of 2.110 nm. Table 2 shows a summary of their distinctive morphological characterisation. The pore diameters indicate that both samples predominantly contain micropores, which are advantageous for charge storage. By implication, they have more available sites for ion adsorption and greater electrolyte accommodation. The BET and BJH analysis results demonstrate that NaOH-HAC outperforms KOH-HAC regarding surface area and pore volume, making it a more viable material for supercapacitor electrodes. The presence of micropores in both samples further contributes to their suitability for energy storage applications.

3.2. Electrochemical Analysis Results

The electrochemical analysis of the supercapacitor material provides insights into its performance characteristics, including capacitance, energy and power densities, impedance behaviour, and charge-discharge efficiency. Below is a discussion of the key results and their implications:
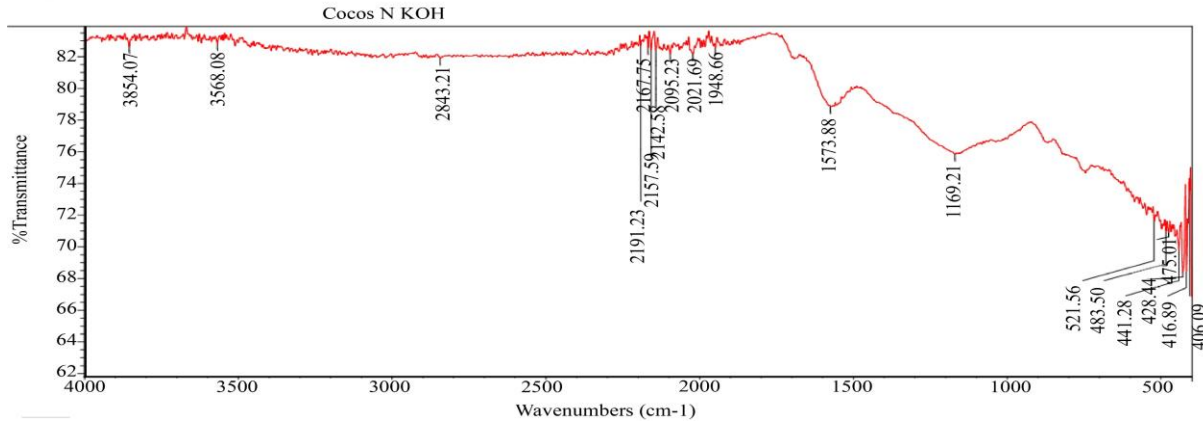

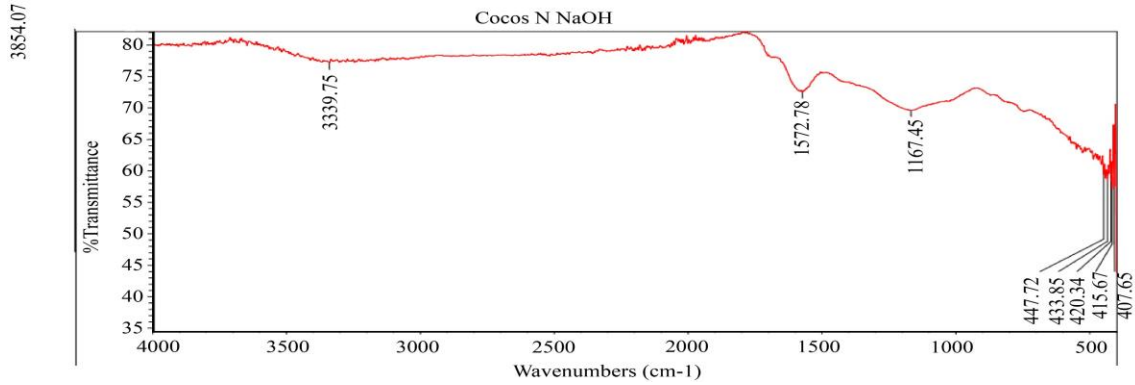**Fig. 7a FTIR spectra for KOH-HAC**
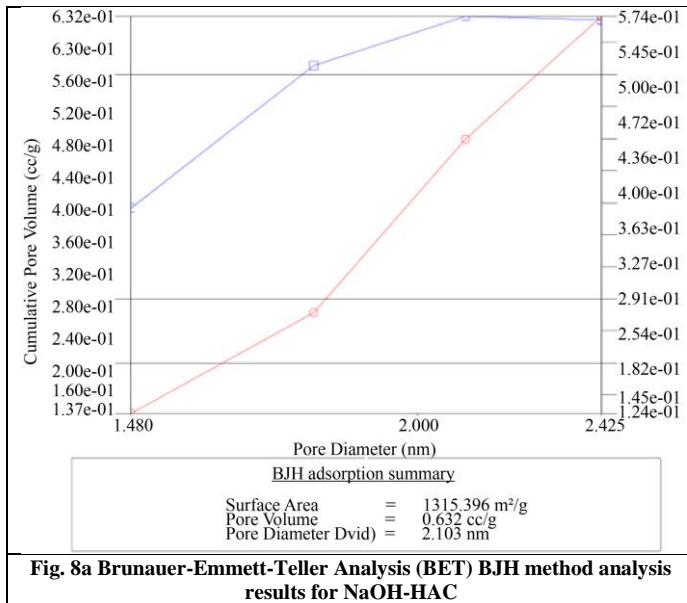
Fig. 7b FTIR spectra for NaOH-HAC

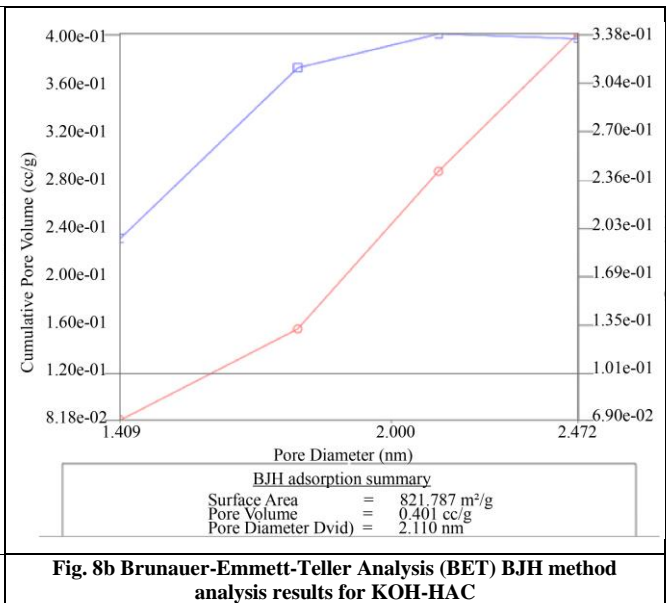| Fig. 8a Brunauer-Emmett-Teller Analysis (BET) BJH method analysis results for NaOH-HAC	Fig. 8b Brunauer-Emmett-Teller Analysis (BET) BJH method analysis results for KOH-HAC

3.2.1. Nyquist Plot Analysis

The Nyquist plot, Figure 8, indicates the impedance characteristics of the material. In this study, at the high-frequency zone, the semicircle depicts the charge transfer resistance, with a peak actual impedance value of 11.51 Ω. This indicates moderate resistance to ion transfer. The near-vertical tail on the right-hand side suggests capacitive behaviour at the low-frequency region, highlighting good ion diffusion and charge storage capabilities at low frequencies. This plot is characteristic of materials with decent capacitive properties and moderate charge transfer resistance, suitable for supercapacitor applications.

3.2.2. Cyclic Voltammetry (CV) Analysis

From Figure 9, the current response is relatively symmetric around the midpoint of the voltage range, indicating good electrochemical stability and consistent capacitive behaviour. A peak near the onset potential of 0.505 V is visible, indicating redox activity. This suggests some pseudocapacitive contribution in addition to Electric Double-Layer Capacitance (EDLC). This behaviour enhanced the

material's overall capacitance and energy storage capability. The CV plot confirms that the material shows promising electrochemical behaviour, with the potential for high capacitance and good charge-discharge efficiency.
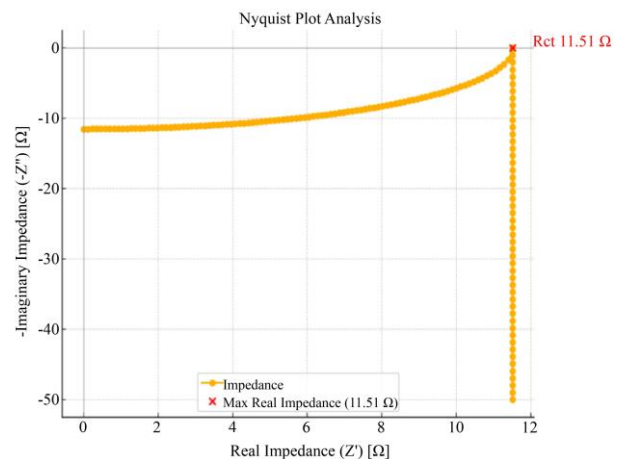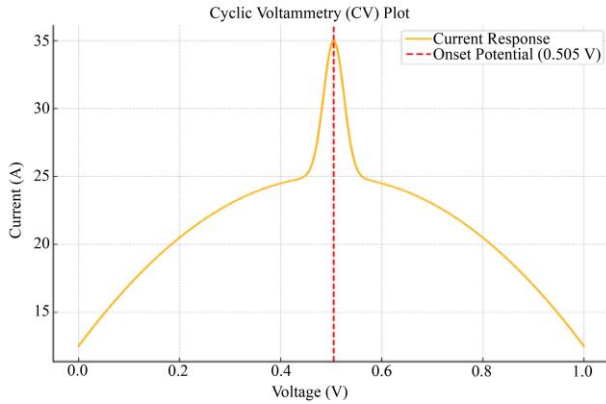

Fig. 9 Nyquist plot
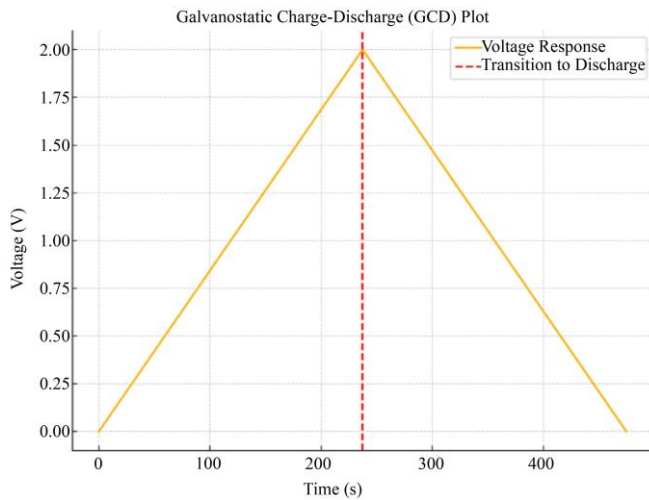
Fig. 10 Cyclic Voltammetry (CV) Curve

Fig. 11 Galvanostatic Charge-Discharge (GCD) Curve

3.2.3. Galvanostatic Charge-Discharge (GCD) Analysis
From Figure 10, the voltage decreases linearly during discharge, indicating minimal resistive losses and ideal capacitive behaviour. The charge-discharge time of 474.75 seconds at a scan rate of 5 mV/s corresponds to 474.75 F/g being the specific capacitance, reflecting the material's ability to store a large amount of charge. The voltage decreases linearly during the discharge phase, indicating ideal capacitive behaviour with minimal resistive losses. The total charge-discharge cycle takes 474.75 seconds, which reflects a high specific capacitance (474.75 F/g). This indicates the material's ability to store and release a significant amount of charge. This GCD plot shows that the material is highly efficient in energy storage, which is a desirable property for supercapacitors.

Table 3 compares various biomass-derived carbon materials used in supercapacitors, focusing on synthesis methods, structural characteristics, and electrochemical properties. The data indicate that carbon derived from coconut shells demonstrates superior performance in specific capacitance, energy density, and power density, making it especially suitable for applications requiring high energy and power outputs. A general trend shows that larger specific surface areas often correspond to higher capacitances, as seen with materials like banana peels and coconut shells. However, electrolyte type and pore size distribution are also critical factors. Commonly used electrolytes include KOH and Na_2SO_4, with KOH often linked to higher specific capacitance, likely due to its high conductivity and strong interaction with carbon materials. This comparison underscores the potential of biomass-derived carbons as sustainable, cost-effective materials for supercapacitors. Optimizing specific capacitance, energy, and power density involves careful selection of the biomass source, activation method, and electrolyte. Coconut shell-derived carbon, in particular, stands out due to its exceptional electrochemical properties, positioning it as a promising candidate for further development in energy storage applications.

Table 3. Comparative Analysis of Electrochemical Capacitors Made of Bio-based Activated Carbon Electrodes in Aqueous Electrolytes

Author	Biomass Source	Synthesis Method	Pore Specific Area (m^2/g)	Electrolyte	Specific Capacitance (F/g)	Energy Density (Wh/kg)	Power Density (W/kg)	Current Density (A/g)
[32]	Ricinus communis shells	KOH Activation, Pyrolysis	1150.00	3 M KOH	137.00	18.20	663.40	1.00
[33]	Pomelo peels	KOH Chemical Activation	1250.00	Na_2SO_4-NaI-KI	215.00	10.50	1400.00	0.50
[34]	Peanut shells	Hydrothermal, KOH Activation	980.00	1 M KOH	247.00	N/A	N/A	0.25
[35]	Banana peels	Carbonization, N-doping	1345.00	1 M Na_2SO_4	302.00	17.60	1245.00	0.80
[36]	Chicken bones	Pyrolysis, N-doping	1285.00	6 M KOH	195.00	15.20	1100.00	1.00
This Study	Coconut shell	Hybrid of Physical and Chemical Activation	1315.40	1 M KOH	474.75	20.00	4500.00	0.80

3.3. Environmental Footprint Assessment

In the chemical activation process using bio-based materials, potassium hydroxide (KOH) and sodium hydroxide (NaOH) are employed to produce activated carbon with high porosity and surface area. The bio-based material (Coconut Shell) is mixed with KOH or NaOH after the physical activation. The alkali hydroxides are typically dissolved in water, and the bio-material is soaked in this solution. The hydroxides diffuse into the material's structure, reacting with organic compounds in the bio-material. During the initial heating stages, the bio-material undergoes dehydration.

This removes water content, opening up the structure and setting the stage for carbonization. The impregnated material is then heated to a high temperature under an inert atmosphere (like nitrogen). At these temperatures, the KOH or NaOH reacts with the carbon in the bio-material, releasing gases like CO, CO_2, and H_2O. This process helps to etch away some carbon atoms, creating a network of pores within the material. As the temperature increases, the reactions intensify, forming micropores, mesopores, and even some macropores in the carbon structure. The alkali hydroxides also help remove tar and other volatile impurities from the carbon matrix.

These reactions further develop the porosity, making the activated carbon highly porous with a larger surface area. After activation, the material is cooled down, and the residues of KOH or NaOH are removed by thorough washing with distilled water or an acidic solution (often HCl) to neutralize any remaining alkali and remove soluble salts. This step is crucial to obtain high-purity activated carbon without residual metal ions. The resulting activated carbon is characterized by a high surface area and a well-developed porous structure, making it highly suitable for electrochemical energy storage, adsorption, and catalysis applications. The carbonization process releases gases like CO_2 and CO. If the process is not optimized or emissions are not controlled, it could contribute to atmospheric pollution and climate change. Despite these impacts, the process can still be eco-friendly if carefully managed and optimized for reduced chemical use, energy efficiency, and effective waste management.

3.4. Cost-Effectiveness Evaluation of the Hybrid Physical and Chemical Activation Strategy Using KOH and NaOH on Coconut Shells

The hybrid activation strategy, employing KOH and NaOH as chemical agents and high-temperature physical activation, is widely used for producing porous carbon materials from coconut shells for supercapacitors. While this method enhances the electrochemical performance of the carbon material, evaluating its cost-effectiveness is essential for assessing its viability at an industrial scale. This assessment considers raw material costs, chemical expenses, energy consumption, waste management, and overall efficiency.

This activation strategy on coconut shells is cost-effective, particularly when considering the high-performance qualities of the resulting carbon material. Using waste coconut shells as a renewable feedstock, combined with the relatively low costs of KOH and NaOH, makes the process economically viable.

The initial energy and chemical costs are offset by the high market value of the final product and potential savings through chemical recycling and renewable energy integration. With proper waste management and process optimization, this activation strategy offers a balanced approach to producing cost-effective, high-performance carbon materials for energy storage applications.

3.5. Scalability and Commercial Viability of the Hybrid Physical and Chemical Activation Process Using KOH and NaOH on Coconut Shells

Scaling up the hybrid physical and chemical activation process using KOH and NaOH with coconut shells as a feedstock offers significant commercial potential, especially in the growing market for sustainable energy storage materials like supercapacitors. However, important considerations related to infrastructure, resource requirements, production efficiency, and market demand influence the scalability and commercial viability of this process. The hybrid physical and chemical activation process using KOH and NaOH on coconut shells is scalable and commercially viable, particularly in regions with abundant coconut shell supplies and access to reliable chemical and energy sources.

Although scaling has challenges, such as waste management, regulatory compliance, and high initial capital investment, the growing demand for sustainable and high-performance carbon materials in energy storage applications makes this process economically attractive. With advancements in automation, waste recycling, and energy efficiency, this process can offer a cost-competitive, eco-friendly solution for producing supercapacitor-grade carbon materials on a commercial scale.

3.6. Applications of Coconut Shell-Derived Activated Carbon in Supercapacitors and Performance Comparisons

Coconut shell-derived activated carbon is a viable material for supercapacitor applications across various sectors, owing to its balance of performance, cost-effectiveness, and environmental sustainability. Although it may not match the highest specific capacitance or energy density in advanced materials like graphene or carbon nanotubes, its high power density, cycle life, and low production cost make it a competitive option. As a renewable biomass source, coconut shell-derived carbon offers an environmentally friendly alternative, particularly for applications where cost and sustainability are essential. As such, it has strong commercial potential in automotive, renewable energy, consumer electronics, industrial, and

medical applications where reliable power delivery is required.

4. Conclusion

The NaOH-HAC derived from coconut shell biomass showcases exceptional electrochemical properties, positioning it as a highly promising candidate for supercapacitor electrodes. It delivers an impressive specific capacitance of 474.75 F/g, with well-balanced energy, power densities, and adequate electrical conductivity. These characteristics make NaOH-HAC particularly suitable for energy storage systems requiring high energy and power capabilities. This study emphasizes the significance of the hybrid activation process, where NaOH serves as an effective activating agent, substantially enhancing the carbon material's surface area and pore structure. Specifically, NaOH-HAC achieves an improved surface area of 1315.396 m²/g and a total pore volume of 0.632 cc/g, surpassing that of KOH-activated carbon. This enlarged surface area, optimized pore distribution, and superior conductivity support efficient ion transport and charge storage, resulting in outstanding electrochemical performance. The synergistic combination of high surface area, well-defined pore architecture, and improved conductivity positions NaOH-HAC as a strong contender for next-generation supercapacitors, paving the way for advanced energy storage technologies that align with the demand for high-performance, sustainable solutions.

References

[1] Silvia Roldán et al., "Mechanisms of Energy Storage in Carbon-Based Supercapacitors Modified with a Quinoid Redox-Active Electrolyte," *Journal of Physical Chemistry C*, vol. 115, no. 35, pp. 17606-17611, 2011. [CrossRef] [Google Scholar] [Publisher Link]

[2] Zhengdao Pan et al., "Recent Advances in Porous Carbon Materials as Electrodes for Supercapacitors," *Nanomaterials*, vol. 13, no. 11, p. 1744, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[3] Joel Brain Njewa, Ephraim Vunain, and Timothy Biswick, "Synthesis and Characterization of Activated Carbons Prepared from Agro-Wastes by Chemical Activation," *Journal of Chemistry*, vol. 2022, no. 1, pp. 1-13, 2022. [CrossRef] [Google Scholar] [Publisher Link]

[4] Mohamad Ezzedine El Dandachy et al., "Effect of Elevated Temperatures on Compressive Strength, Ultrasonic Pulse Velocity, and Transfer Properties of Metakaolin-Based Geopolymer Mortars," *Buildings*, vol. 14, no. 7, pp. 1-21, 2024. [CrossRef] [Google Scholar] [Publisher Link]

[5] O. Ioannidou, and A. Zabaniotou, "Agricultural Residues as Precursors for Activated Carbon Production—A Review," *Renewable and Sustainable Energy Reviews*, vol. 11, no. 9, pp. 1966-2005, 2007. [CrossRef] [Google Scholar] [Publisher Link]

[6] Lakshana G. Nair, Komal Agrawal, and Pradeep Verma, "An Overview of Sustainable Approaches for Bioenergy Production from Agro-industrial Wastes," *Energy Nexus*, vol. 6, pp. 1-25, 2022. [CrossRef] [Google Scholar] [Publisher Link]

[7] Panagiota Paraskeva, Dimitrios Kalderis, and Evan Diamadopoulos, "Production of Activated Carbon from Agricultural By-Products," *Journal of Chemical Technology and Biotechnology*, vol. 83, no. 5, pp. 581-592, 2008. [CrossRef] [Google Scholar] [Publisher Link]

[8] Muhammad Saleem, "Possibility of Utilizing Agriculture Biomass as a Renewable and Sustainable Future Energy Source," *Heliyon*, vol. 8, no. 2, pp. 1-11, 2022. [CrossRef] [Google Scholar] [Publisher Link]

[9] Osarhiemhen Azeta et al., "A Review on the Sustainable Energy Generation from the Pyrolysis of Coconut Biomass," *Scientific African*, vol. 13, pp. 1-14, 2021. [CrossRef] [Google Scholar] [Publisher Link]

[10] Rabi Kabir Ahmad et al., "Exploring the Potential of Coconut Shell Biomass for Charcoal Production," *Ain Shams Engineering Journal*, vol. 13, no. 1, pp. 1-13, 2022. [CrossRef] [Google Scholar] [Publisher Link]

[11] Yong X. Gan, "Activated Carbon from Biomass Sustainable Sources," *C Journal of Carbon Research*, vol. 7, no. 2, pp. 1-33, 2021. [CrossRef] [Google Scholar] [Publisher Link]

[12] Kuan-Ching Lee et al., "Coconut Shell-Derived Activated Carbon for High-Performance Solid-State Supercapacitors," *Energies*, vol. 14, no. 15, pp. 1-11, 2021. [CrossRef] [Google Scholar] [Publisher Link]

[13] Yawei Wang et al., "Hierarchical Porous Activated Carbon Derived from Coconut Shell for Ultrahigh-Performance Supercapacitors," *Molecules*, vol. 28, no. 20, pp. 1-14, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[14] Zoha Heidarinejad et al., "Methods for Preparation and Activation of Activated Carbon: A Review," *Environmental Chemistry Letters*, vol. 18, pp. 393-415, 2020. [CrossRef] [Google Scholar] [Publisher Link]

[15] Joseph Jjagwe et al., "Synthesis and Application of Granular Activated Carbon from Biomass Waste Materials for Water Treatment: A Review," *Journal of Bioresources and Bioproducts*, vol. 6, no. 4, pp. 292-322, 2021. [CrossRef] [Google Scholar] [Publisher Link]

[16] Md Sumon Reza et al., "Preparation of Activated Carbon from Biomass and Its' Applications in Water and Gas Purification, A Review," *Arab Journal of Basic and Applied Sciences*, vol. 27, no. 1, pp. 208-238, 2020. [CrossRef] [Google Scholar] [Publisher Link]

[17] C. Sarathchandran et al., "Activated Carbon: Synthesis, Properties, and Applications," *Handbook of Carbon-Based Nanomaterials*, pp. 783-827, 2021. [CrossRef] [Google Scholar] [Publisher Link]

[18] Asif Ali, Ning Zhang, and Rafael M. Santos, "Mineral Characterization Using Scanning Electron Microscopy (SEM): A Review of the Fundamentals, Advancements, and Research Directions," *Applied Sciences*, vol. 13, no. 23, pp. 1-33, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[19] Nadeem Joudeh, and Dirk Linke, "Nanoparticle Classification, Physicochemical Properties, Characterization, and Applications: A Comprehensive Review for Biologists," *Journal of Nanobiotechnology*, vol. 20, pp. 1-29, 2022. [CrossRef] [Google Scholar] [Publisher Link]

[20] Gopalakrishnan Kothandam et al., "Recent Advances in Carbon-Based Electrodes for Energy Storage and Conversion," *Advanced Science*, vol. 10, no. 18, pp. 1-50, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[21] Bhumika Tiwari et al., "Synergistic Combination of N/P Dual-doped Activated Carbon with Redox-active Electrolyte for High Performance Supercapacitors," *Journal of Physics and Chemistry of Solids*, vol. 161, 2022. [CrossRef] [Google Scholar] [Publisher Link]

[22] Uttam Kumar et al., "Extraordinary Supercapacitance in Activated Carbon Produced Via a Sustainable Approach," *Journal of Power Sources*, vol. 394, pp. 140-147, 2018. [CrossRef] [Google Scholar] [Publisher Link]

[23] P. Sivaraman et al., "All Solid Supercapacitor Based on Polyaniline and Crosslinked Sulfonated Poly [Ether Ether Ketone]," *Electrochimica Acta*, vol. 55, no. 7, pp. 2451-2456, 2010. [CrossRef] [Google Scholar] [Publisher Link]

[24] Ayesha Kausar et al., "Green-Synthesized Graphene for Supercapacitors—Modern Perspectives," *Journal of Composites Science*, vol. 7, no. 3, pp. 1-21, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[25] Er-Tai Liu et al., "Conducting Polymers with Redox Active Pendant Groups: Their Application Progress as Organic Electrode Materials for Rechargeable Batteries," *Journal of Material Chemistry C*, vol. 10, pp. 13570-13589, 2022. [CrossRef] [Google Scholar] [Publisher Link]

[26] Meir S. Yerdauletov et al., "Characterization of Activated Carbon from Rice Husk for Enhanced Energy Storage Devices," *Molecules*, vol. 28, no. 15, pp. 1-12, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[27] Nonjabulo P.D. Ngidi, Andrei F. Koekemoer, and Siyabonga S. Ndlela, "Recent Advancement in the Electrochemical Performance of Electrochemical Capacitors based on Biomass-Derived Porous Carbon: A Review," *Journal of Energy Storage*, vol. 89, pp. 1-25, 2024. [CrossRef] [Google Scholar] [Publisher Link]

[28] Akhil Pradiprao Khedulkar et al., "Sustainable High-energy Supercapacitors: Metal Oxide-agricultural Waste Biochar Composites Paving the Way for a Greener Future," *Journal of Energy Storage*, vol. 77, pp. 1-17, 2024. [CrossRef] [Google Scholar] [Publisher Link]

[29] Vaddi Dhilleswara Rao et al., "Efficient Biosorption of Cadmium Ions from Wastewater using Iron Oxide–maize Shell Activated Bio-Carbon Nanocomposites," *Biomass Conversion and Biorefinery*, 2024. [CrossRef] [Google Scholar] [Publisher Link]

[30] Cheng Rong et al., "High-performance Supercapacitor Electrode Materials from Composite of Bamboo Tar Pitch Activated Carbon and Tannic Acid Carbon Quantum Dots," *Journal of Energy Storage*, vol. 95, 2024. [CrossRef] [Google Scholar] [Publisher Link]

[31] Keiko Ideta et al., "A Quantitative Evaluation of the Large Pore-size Effect on the Electric Double-layer Capacitance for High Voltage by 19F-NMR," *Carbon*, vol. 214, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[32] Sofia Jeniffer Rajasekaran et al., "Investigation of Different Aqueous Electrolytes for Biomass-Derived Activated Carbon-Based Supercapacitors," *Catalysts*, vol. 13, no. 2, pp. 1-13, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[33] Nghia Trong Nguyen, P.A. Le, and Viet Bac T. Phung, "Biomass-derived Activated Carbon Electrode Coupled with a Redox Additive Electrolyte for Electrical Double-layer Capacitors," *Journal of Nanoparticle Research*, vol. 22, 2020. [CrossRef] [Google Scholar] [Publisher Link]

[34] T. Manimekala et al., "Biomass Derived Activated Carbon-based High-performance Electrodes for Supercapacitor Applications," *Journal of Porous Materials*, vol. 30, pp. 289-301, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[35] Yongpeng Ma et al., "Recent Advances in the Application of Carbon-based Electrode Materials for High-performance Zinc Ion Capacitors: A Mini Review," *Advanced Composites and Hybrid Materials*, vol. 6, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[36] Delvina Japhet Tarimo et al., "Waste Chicken Bone-derived Porous Carbon Materials as High Performance Electrode for Supercapacitor Applications," *Journal of Energy Storage*, vol. 51, 2022. [CrossRef] [Google Scholar] [Publisher Link]