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Activation of biomass precursors and chemical preparation of hierarchical porous carbons for supercapacitor applications

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ABSTRACT

Growing population in the world demands more accumulation of energy. Among the storage devices, capacitors have triggered enormous interest due to its excellent electrochemical characteristics. Activated carbon electrodes from Africana Duranta, Tectona Grandis, and Terminalia Catappa carbon waste, have attracted high interest because of high specific surface area and an abundant pore volume with rational micro/meso pores. The carbon black samples were prepared by a simple green synthesis with KOH treatment followed by pyrolysis method. XRD confirmed the amorphous carbon black allotrope of the carbon black respectively. The carbon obtained from the leaf, Africana Duranta showed high surface area in the range of 9.08 m²/g - 28.592 m²/g with pore radius in the range of 16.768 Å – 877.4509 Å, which was found from BJH and BET analysis respectively. Then the specific capacitance values were calculated from the CV curves using electrochemical analyzer. The highest specific capacitance value of 83.58 Fg^{-1} was found for Africana Duranta, which was mainly due to high surface area compared to other two leaves.

Keywords: Capacitors; Biomass derived carbon black; Africana Duranta

1. INTRODUCTION

There are numerous efforts have been made in electrochemical energy generation/ storage/conversion devices such as lithium or sodium ion batteries electrochemical capacitors, fuel cells, hydrogen generation from electrolysers and metal air batteries to ease the energy and environmental challenges. Supercapacitors (SC) are one of the well-thought-out to be a constructive devices Supercapacitors are a leading energy storage technology of the new generation because of its many advantages, which include a long lifespan, an ultra-fast charge/discharge rate, and a moderate energy density [1] One of the most promising energy storage technologies is the supercapacitor, which outperforms batteries in several ways, including high power density, strong cycle performance, and high rate performance. [2], A novel kind of energy storage technology, supercapacitors in which it is Equipped with superior cycle stability, high power density, and high energy density, they offer all the benefits of traditional capacitors and batteries [3]. The cleanness, high efficiency, and environmental friendliness of supercapacitors are further appealing qualities that set them apart from other forms of energy storage. Graphene, carbon nanotubes, and porous carbon are examples of carbonaceous materials that have shown a lot of promise for supercapacitor applications due to their high specific capacitance, extended service life, and superior chemical stability the largespecific surface area, customizable pore structure, superior electrical conductivity, and low synthesis cost of porous carbon provide it with strong competitive advantages over graphene and carbon nanotube [4]. The development of hierarchical porous carbon (HPC), which is regarded as one of the best electrode materials for SCs because to its three-dimensional (3D) porous channels with a well-balanced micro-, meso-, and microporous structure, opened the door to new topologies with one step activation using KOH This study offers a unique methodfor generating pores and preserving the precursor's intrinsic textural qualities that attract electrochemically. By using this workable approach, it is possible to create a 3D architecture with a porous carbon hierarchical structure and a substantial specific surface area [5], To provide a significant advancement in industrial applications, it is necessary to find inexpensive and ecologically safe precursors that can preserve their original textural qualities and electrochemical attraction while producing hierarchical porous carbons with outstanding electrochemical performance [6]. Porous carbon has been prepared by chemically and physically activating biomass and biowaste at high temperatures Innovation in the production of materials with biomass will help to solve upcoming energy-related issues. Transforming garbage into treasure, the current project involves preparing porous carbon from Leaves, the impact of chemical pre-treatment time on the chemistry of activated carbons made from biomass from Africana Duranta, Terminalia catappa, Tectona Grandis leaves was investigated in order to improve process and property control. By adjusting the pre-treatment time, it was possible to manage the microstructure, chemistry, and active functional groups while also removing certain hemicellulose and lignin concentrations and preventing early pore growth. The best KOH pre-treatment, which took 12–18 hours, produced interconnected pore structure [7-10] With this knowledge, the pore network, chemistry, and ultimate performance of the porous activated carbon supercapacitor electrodes may be easily and affordably controlled [11] producing abundant porosity activated carbon employing a sustainable synthesis process without the need for carbon material templates derived from biowaste. These waste carbons are abundant, cheap, and naturally recyclable carbon precursors [12].

2. MATERIALS USED FOR SYNTHESIS

Dried leaves of Tectona Grandis, and Terminalia catappa, Africana Duranta, Ethanol, KOH , HCL, DI water , chemicals which are of analytical grade from Fisher Scientifics , Whatman Grade 41 filter paper which has a pore size of 20–25 microns for filtration, Nitrogen purged tubular furnace under controlled temperature conditions in order to avoid explosion , Hydrothermal autoclave . Transparent conductive metal oxide known as FTO (Fluorine-doped Tin Oxide) glass are utilized to create transparent electrodes. FTO substrate for measuring electrochemical performance of prepared activated porous carbon electrodes.

3. CHARACTERISATION

The materials surface morphology was examined using a scanning electron microscope (SEM, Carl Zeiss). Quantachrome N2 adsorption-desorption were used to analyse the pore structure. The mesopore volume and pore diameter were determined using the Barrett-Joyner-Halenda (BJH) technique, the data, and the Brunauer-Emmett-Teller (BET) method. Carbon confirmation via X-ray Diffraction (XRD).

4. EXPERIMENTAL SECTION

Leaves of Africana Duranta, Tectona Grandis ,and Terminalia catappa were collected which is widely grown in the south India geographical regions and washed with DI water and ethanol to remove the impurities and kept it in hot air oven for drying 8 hours at 80^0 c then the leaveswere ground for 6 hours it is subjected to activation by using KOH in which 6M KOH is prepared 20 gm of biomass samples is taken in 100ml of 6M KOH and kept in hydrothermal autoclave in hot air oven then Biochar is prepared then it is dried in magnetic stirrer for 5 hours then it is again finely ground for 6 hours and kept in tubular furnace with the flow of nitrogen under controlled temperature at the rate of 5^0 C per minute and holding time of 4 hours at 750^0 c in alumina crucible , Chemical activation is accomplished in two steps, the biomass material is pyrolyzed to create a char, which is then impregnated with the chemical activation agent. The impregnated char is then activated at a high temperature to generate activated carbon.

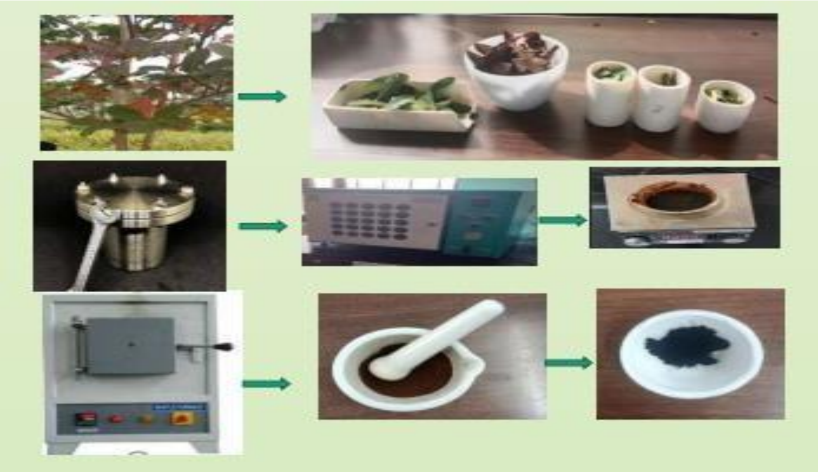


Figure 1. Flowchart of the preparation of carbon black via green synthesis followed bypyrolysis method.

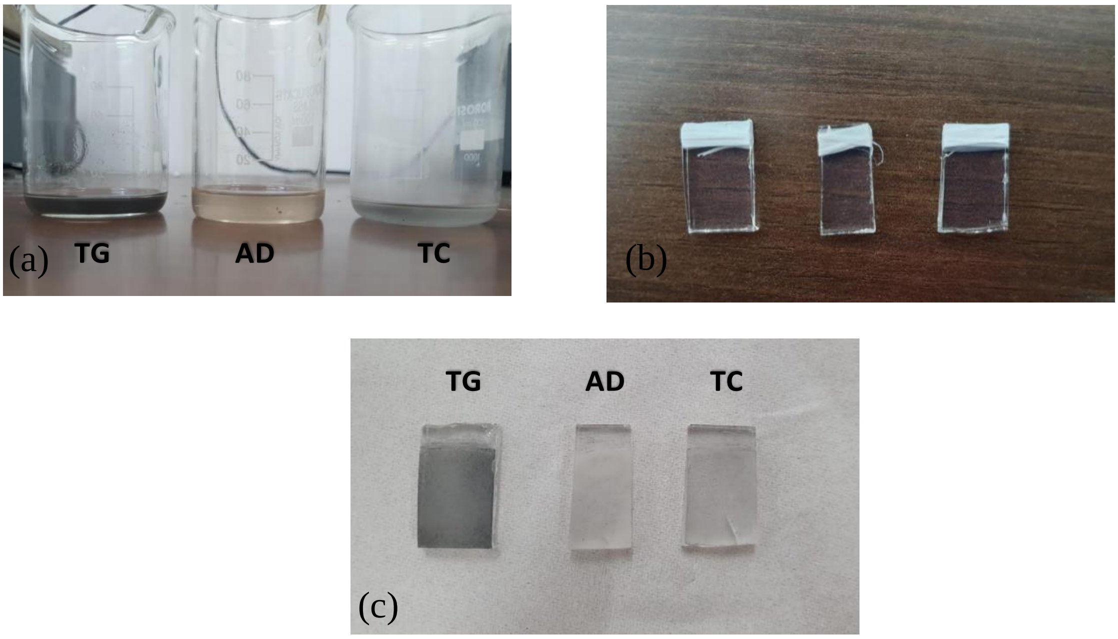


Figure 2. (a) colloidal solutions of TG,AD and TC respectively. (b) FTO glass substrate with Teflon tape wrapped on one edge before coating. (c) After coating the carbon black on FTO via drop casting method.

Colloidal suspension was prepared by taking 4 mg of activated carbon, which was prepared from three different leaves in 10 ml of isopropanol which was shown in figure 1, then using FTO substrate(figure2) which is conductive in nature, all three suspensions were coated with10 layers by keeping FTO on hot plate at 100 ◦C using three different droppers. After coating the samples were let to dry and come to room temperature (Figure 3), and subjecting these samples for electrochemical performance.

5. RESULTS AND DISCUSSIONS

5.1.XRD Analysis

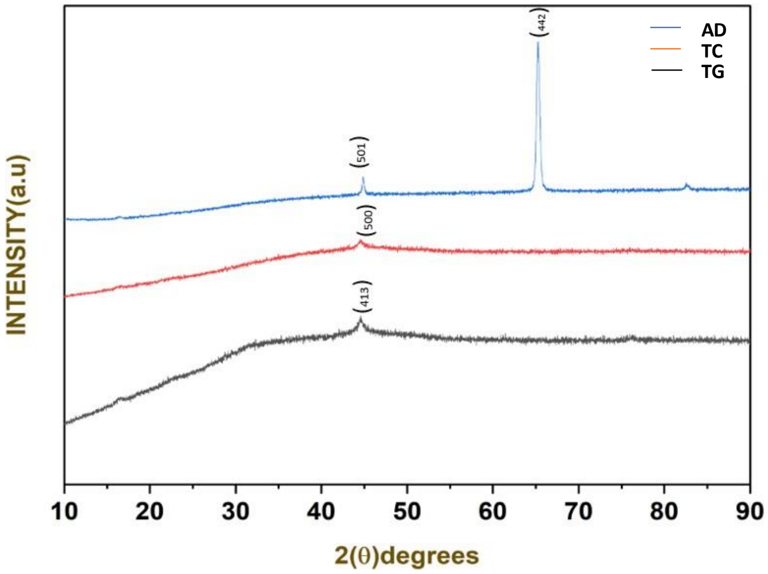
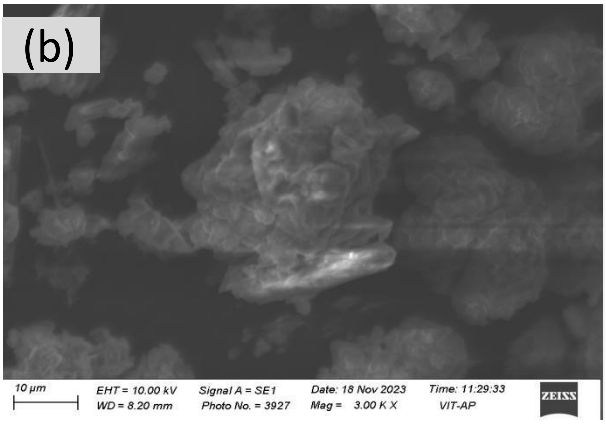


Figure 3. XRD spectra of Africana duranta, Terminalia catappa and Tectona grandis

Activated carbon from the leaves of Africana Duranta, Terminalia catappa, Tectona Grandis was subjected to X-ray diffraction examination (XRD) to ascertain its crystallinity or amorphous nature. The investigation was carried out utilizing a Cu-Kα radiation source running at 30 kV and 23 mA in the D2 Phaser X-ray diffractometer. The range of the diffraction angle(2θ) was 10º to 90º. The scan rate used to gather the X-ray diffraction patterns was 5.2ºC/min.

We observed a peak at 44 degrees for all the precursor Africana Duranta (AD), Terminalia catappa (TC), Tectona Grandis (TG) which confirms the activated carbon. Africana Duranta peaked which the cellulose peaks are responsible for. Furthermore, an extensive peak within the 44-45 degrees range is described too amorphous. Amorphous carbon is responsible for the large peak seen in the carbonized Tectona Grandis leaf at 69 degrees, other two leaves are not showing the peak at 69 degrees because of the low intensity. Africana Duranta showing peaksat 44.844 degrees and 65.18 degrees Terminalia catappa at 44.53 degrees, Tectona Grandis at 44.546 degrees Respectively confirming the carbon [12]

5.2. Structural analysis using SEM



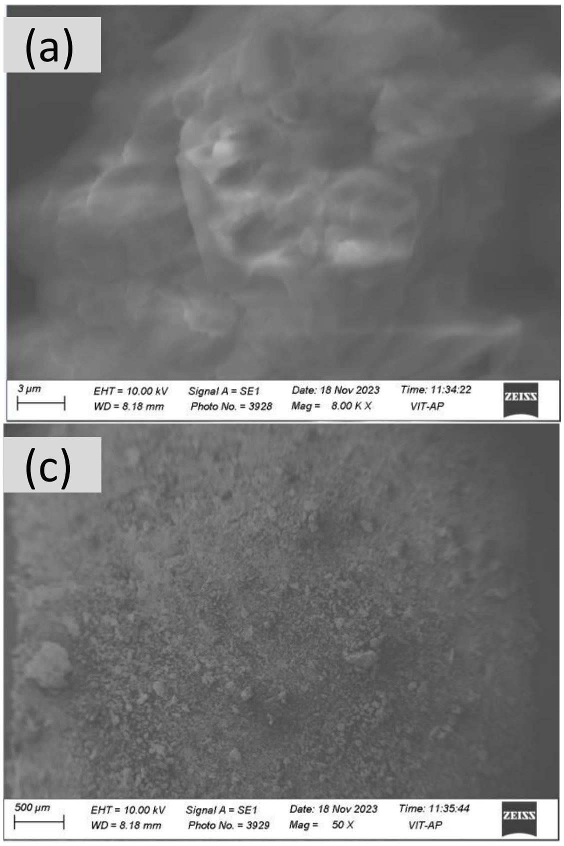


Figure 4. SEM images of carbon black from Africana duranta

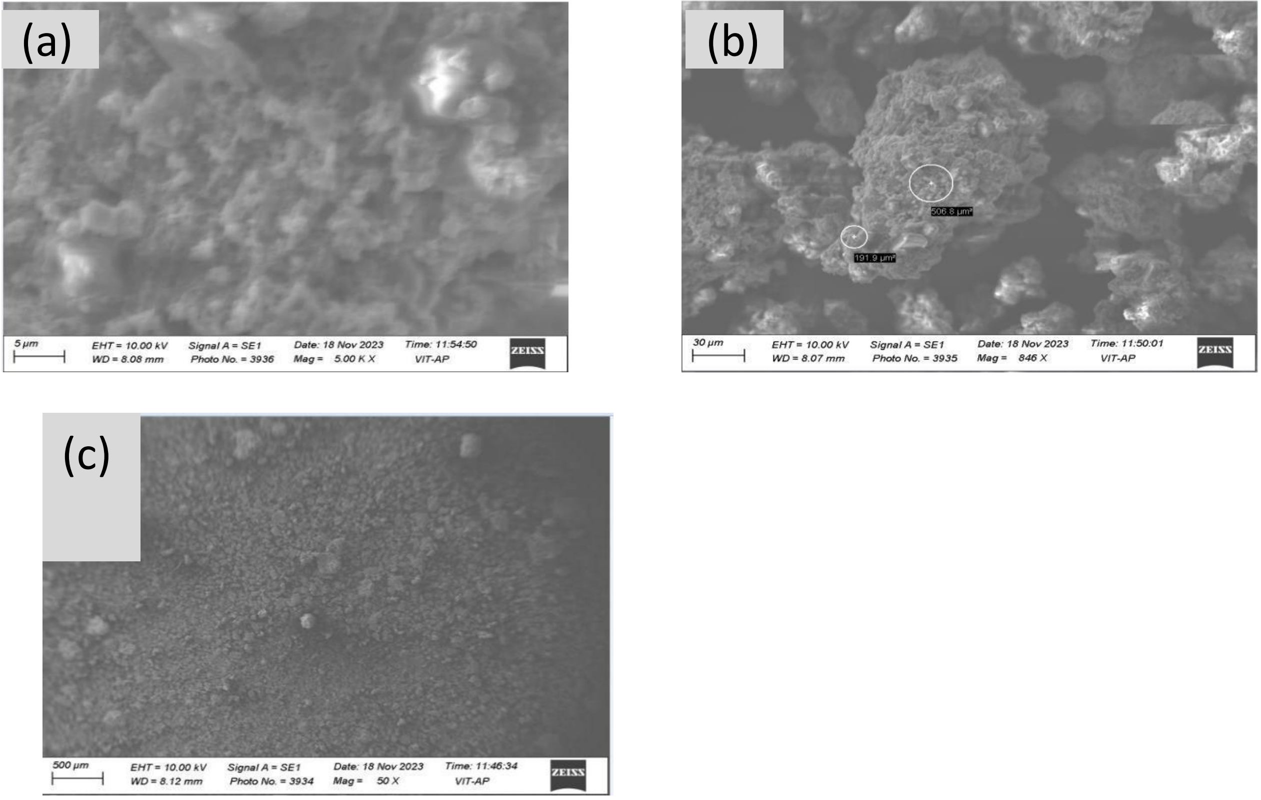


Figure 5. SEM images of carbon black from Tectona grandis

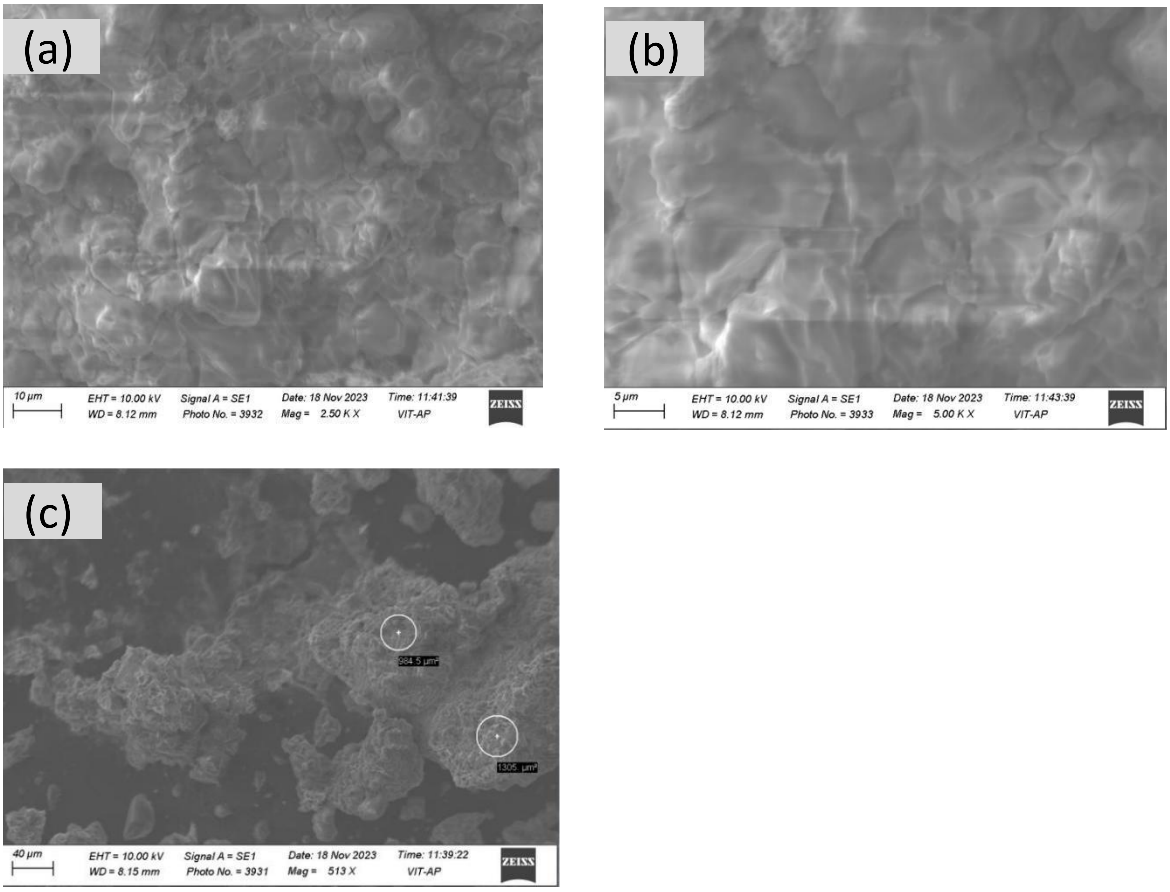


Figure 6. SEM images of carbon black from Terminalia catappa

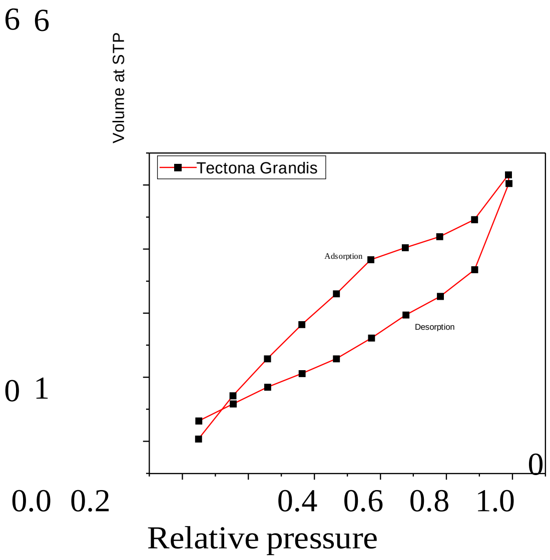
SEM images of Africana Duranta Figure 4 (a, b, c), Tectona Grandis Figure 5 (a, b, c) and Terminalia Catappa Figure 6 (a, b, c) showing the pores, leaves exhibit the carbonization post-activation-induced development of primitive pores in SEM images. The evaporation of impregnated KOH, directly results in the creation of meso cavities and developed pores Figure 8b. There is a non-uniform distribution of pores. The pores have an uneven shape. The pores in Figure 4b. are connected to Circular pores and microscopic fractures begin to form during carbonization in the presence of an inert environment. Figure 5b displays the SEM microstructures of the Terminalia catappa activated carbon pores and shows how pore structure and microstructural development are affected by the length of the chemical pre-treatment. Forevery activated carbon, the low-magnification SEM pictures show three-dimensional structures and coupled porous networks with comparatively thick pore walls in Tectona Grandis Figure 4b. By serving as interfaces for charge storage, these structures may facilitate ion transit. Following a 6-hour chemical preparation, macro pores and micro/mesopores began to develop Figure 5b. Since micropores and meso/micropores often contribute to the creation of electrical double layers and ion storage/diffusion, respectively, a broad pore size distribution is essential. As seen in Figure 5b,6b, a significant amount of micro/mesopores developed around the thickpore walls when the pre-treatment duration was increased from 3 to 4 hours. Substantial morphological and pore structural and high concentration of micro/mesopores encompassed the whole interior area of the plate-like pore walls. This produced a morphology like a layered sheet. The carbonized product's pore structure helps with subsequent activation since it allowsfor the creation of more pores and easier activator penetration due to the bigger contact area which is shown in the SEM images in the Figure (4b,5b,6c) These mesopores have the ability to deliver electrolyte throughout the charging and discharging process, store electrolyte, and reduce the distance of electrolyte diffusion [13]

5.3. BET Analysis

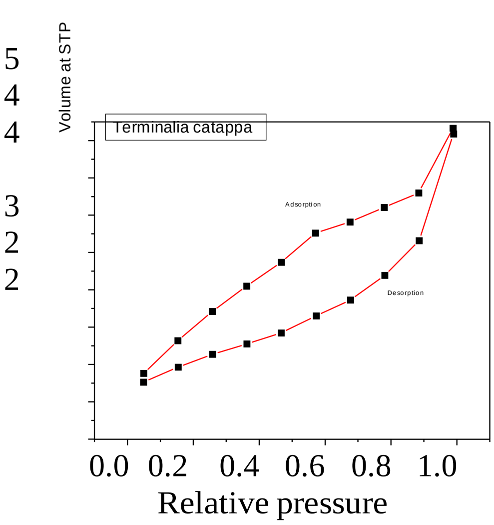
superior surface qualities in terms of surface area and micropore area, according to surface area analysis performed using BET. The effectiveness of KOH as an activating agent in the production of activated carbon with a surface area of up to 28.592m^2/g has been studied , with impregnation being found to be a major influence. It is evident that the hydrothermal process utilizing a chemical activator result in an increase in porosity and surface area. This could be a strong hint that the KOH impregnation acted as a catalyst to promote the formation of porosity. pore structure began to assemble on the surface area following the KOH activation.

BET Analysis at 5-point adsorption and degassing is 300°C for Africana Duranta , Tectona Grandis and Terminalia catappa carbon Using liquid nitrogen, the solid sample's surface areais cooled to cryogenic temperature while operating under vacuum[14]. The solid sample (adsorbent) is dosed with nitrogen gas in regulated increments, as is customary for adsorbates[15]. The sample of Tectona Grandis 0.0595g is taken and is conducted at 77.35K, with liquid density of 0.808g/cc nitrogen is the inert gas used for analysis and conducted for 1hour 39 minutes for adsorption and desorption, and obtained the pore radius with the range of 16.7845Å to 549.7919 Å, the adsorption and gradual desorption in shown in the Figure 4a and Terminalia catappa sample weight of 0.049g is taken with the analysis time of 1 hour 17 minutes at 77.35K with which adsorption curve is increased as the volume and pressure increased and desorption curve is gradually decreased as shown in Figure 4b in which obtained the pore radius ranges from 7.8966 Å to 202.5386 Å, Africana Duranta sample weight of 0.0827g is taken with the temperature of 77.35K and analysis time of 1 hour 38 minutes with adsorption curve started from 1.1cc volume at STP and desorption at 0.01cc as shown in Figure 4c and obtained the pore radius ranging from 16.768 Å to 877.4509 Å is high pore radius on comparison with Tectona Grandis and Terminalia catappa [16,17].

(a)

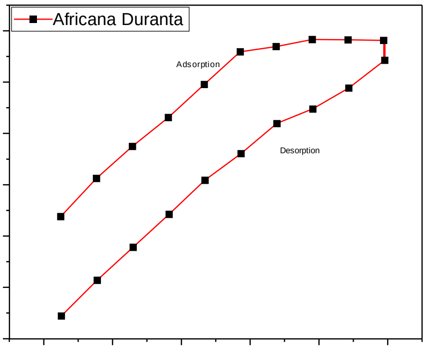


(b)



(c)(c)

3.0



2.5

2.0

1.5

Volume at STP

1.0

0.5

0.0

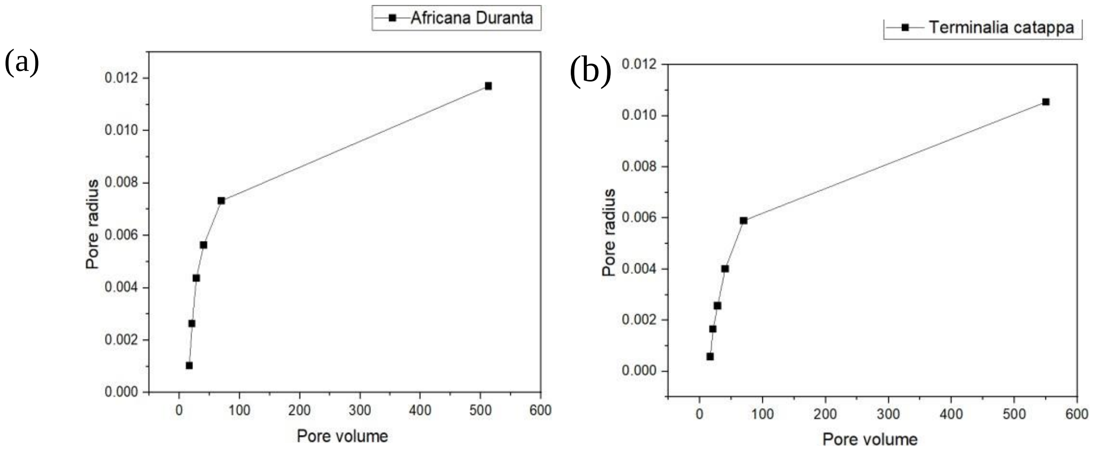
0.0 0.2 0.4 0.6 0.8 1.0

Relative pressure

Figure. 7 BET analysis of (a) TG (b) TC and (c) AD carbon black samples and their respective adsorption and desorption curves.

5.4.BJH Analysis

Improved surface analysis of carbon adsorbents of Bio-mass with which nitrogen molecules it has a range of relative pressure from $6x10^{-7}$ – 0.9895 N/m^2 this work is to obtain the surface area of these Bio-mass, These active carbons subjected to perform under nitrogen adsorption isotherms by varying pressure ,volume and obtained the graphs for pore radius ,pore volume in Figure 8 and the surface area of Africana Duranta , Terminalia Catappa , Tectona Grandis is found to be ranging from 9.08 m²/g - 28.592 m²/g, 8.0974 m²/g-16575 m²/g, 7.2189 m²/g-8.288 m²/g These uneven distributions has been examined by BJH method and in good agreement of adsorption of porosity distribution ,pore radius and surface area foreseeing the specific capacitance of the material as the increase in the pore radius [18],specific capacitance also found to be increased and its high specific capacitance is found for Africana Duranta on comparison to Terminalia catappa , Tectona Grandis ,The activated carbon samples are kept in the nitrogen gas for analysis with bath temperature of 77.35K in void volume of helium measure and warm zone volume at 8.19159cc molecular diameter is 3.54 Å, liquid density of 0.808 g/cc final gas outcome temperature is 373K [18], In Figure 8a,b the pore radius and pore volume increase but in Figure 8c after 3 points of gradual incremental increase it has attained constant pore radius is shown.



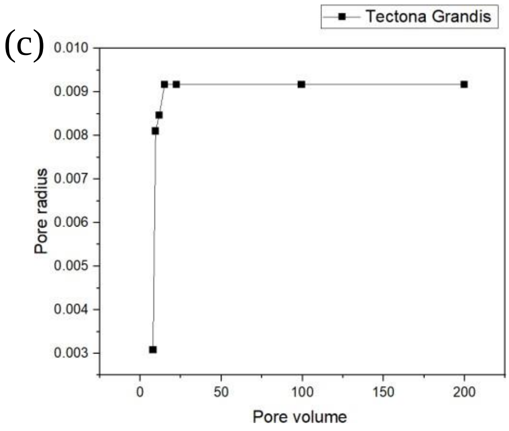


Figure. 8 BJT analysis of (a) AD (b) TC and (c) TG carbon black samples.

6. ELECTROCHEMICAL ANALYSIS

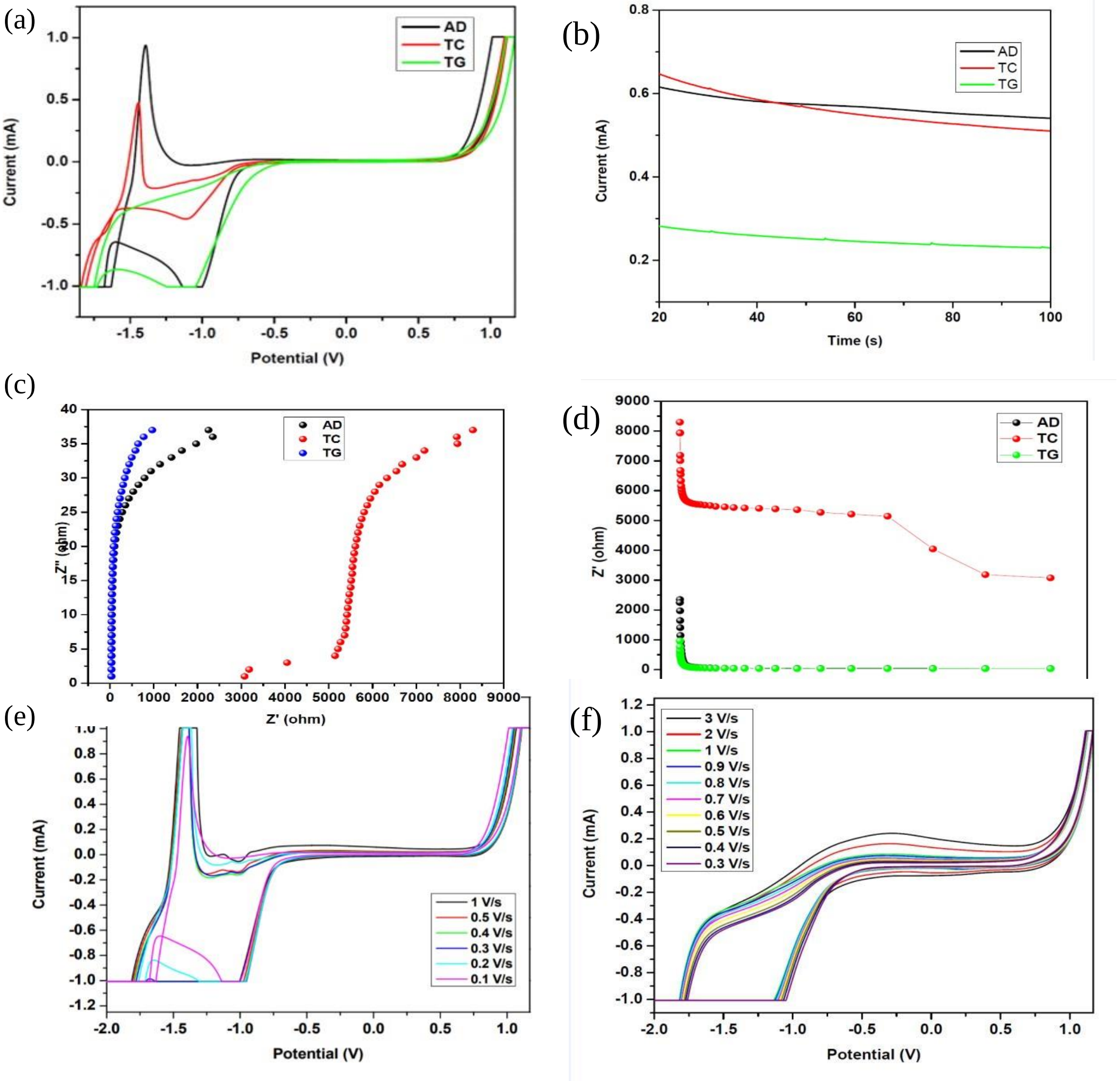


Figure 9. (a) Cyclic Voltammetry (CV) plots of AD, TC and TG samples in 0.1 M NaOH base

solution
(b) IT measurements of AD, Tc and TG samples at 0.1 M NaOH base solution (c) Nyquist plots of AD, TC, and TG samples. (d) Impedance Vs Frequency plots. (e) and (f) CV plots with increasing scan rate from 0.1- 1V/s for AD sample and 0.3 – 3 V/s for TC sample.

Figure(9) shows the current Volta grams of all the three samples at a scan rate of 0.1 V/s in the potential window of -2 to 1.5 V. The area under the CV curve specifies about the capacitance of the samples. The redox peaks were observed in the AD and TC samples but not in the TG sample, which explains the pseudo capacitance was more for AD and TC sample as the total capacitance would be the sum of rectangular and non-rectangular features, that is double layer and pseudo capacitance. This particular redox peak will enhance the charge storage. The pseudocapacitive materials store charge through reversible faradic reactions, which contributes to higher energy density. Specific capacitance was found to be more for Africana Duranta than Tectona Grandis and Terminalia catappa this was mainly due to the higher surface area of the porous carbon obtained from Africana Duranta, which gives more charge storage availability. the values were (AD) 83.58 Fg^{-1},(TG) 14.84 F/g and (TC) 15.70 F/g. The current v/s potential curve is showing high results for Africana Duranta in figure 8. And high resistance peak for Terminalia catappa on comparison with the Africana Duranta leaves and Tectona Grandis as observed in figure 9 (c). Figure 9 (e) and (f) depicts the cv plots with increase in scan rate for both AD and TC samples. There was no deuteriation in the shape of the CV curves was observed, which signifies there was no degradation of the electrodes even at high scan rate. And also, by increasing the scan rates, area of the of the CV curves was also increased. Because at higher scan rates due to high potential charges, the ions might get more active sites on the electrode surface, which increases the charge storage capacity. From figure 9 (d) we observed that the impedance was less for AD and TG samples compared to TC in the frequency range of 0 to 1000 Hz. This tells that at lower frequency the TC sample won't be suitable for capacitive application, due to its low stability to charge and discharge mechanisms. And in turn for AD and TC samples, both at lower and higher frequency the impedance was less, and in turn it would show stable charge and discharge mechanisms. The increase in the impedance was also attributed to more dense layers formed on the FTO compared to AD and TG.

7. CONCLUSIONS

Specific capacitance of the, Terminalia catappa , Africana Duranta ,Tectona Grandis is found to be, 15.70 F/g, 83.58 F/g, 14.84 F/g , High surface area was observed in Africana Duranta leaves, which ranged from 9.08 m²/g to 28.592 m²/g, while pore radius was found to be between 16.768 Å – 877.4509 Å for Africana Duran , 9.49 Å and 125.003 Å for Tectona Grandis , and Terminalia catappa .The carbons derived from the Africana Duranta, Tectona Grandis, Terminalia catappa as sustainable biomass carbon source via direct KOH activation was investigated. Activated carbons with porosity by a Sustainable synthesis method without using templates from a biowaste carbon material. This waste carbon is inexpensive, abundant as well as carbon recyclable natural precursor. With the increase of the magnification abundant pores with different shapes and sizes can be observed on the surface of the material. It is possible to create unique structure porous carbon for high-performance supercapacitors using this convenient method since it is inexpensive and environmentally friendly

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