PREPARATION, CHARACTERIZATION AND APPLICATION OF ACTIVATED CARBON PREPARED FROM WALNUT SHELLS FOR ENERGY HARVESTING

A DISSERTATION SUBMITTED FOR THE PARTIAL FULFILLMENT OF REQUIREMENT OF THE MASTER OF SCIENCE DEGREE IN CHEMISTRY

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BOARD OF EXAMINER AND CERTIFICATE OF APPROVAL

This dissertation entitled, "**Preparation, Characterization and Application of Activated Carbon Prepared from Walnut Shells for Energy Harvesting**" by **Sushila Subedi** under the supervision of **Prof. Dr Armila Rajbhandari**, Department of Chemistry, Central Department, Tribhuvan University, Kathmandu, Nepal, and co-supervision of **Mr. Naresh Prashad pant**, Department of Chemistry, Amrit Campus, Tribhuvan University, Kathmandu, Nepal, hereby submitted has been approved for partial fulfillment of the requirement for completion of her Master of Science (M.Sc.) Degree in Chemistry. This dissertation has not been submitted to any other university or institution previously for the award of a degree.

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LETTER OF RECOMMENDATION

This is to certify that **Ms. Sushila Subedi** has completed M.Sc. thesis entitled **"Preparation, Characterization and Application of Activated Carbon Prepared from Walnut Shell for Energy Harvesting"** as a partial fulfillment of the requirements of an M.Sc. degree in Chemistry under my supervision. To my knowledge, this work has not been submitted for any other degree.

She has fulfilled all the requirements laid down by the Institute of Science and Technology (IOST), Tribhuvan University, Kritipur for the submission of the thesis for the M.Sc. degree.

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DECLARATION

The thesis entitled "**Preparation, Characterization and Application of Activated Carbon Prepared from Walnut Shell for Energy Harvesting"** which is being submitted by me to the Department of Chemistry, Amrit Campus, TU, Kathmandu, Nepal for the Master's degree is a research work carried out by me under the supervision and guidance of Prof. Dr. Armila Rajbhandari (Nyachhyon), Central Department of Chemistry, Tribhuvan University, Nepal and Co-Supervision of Mr. Naresh Prashad Pant, Department of Chemistry, Amrit Campus, TU, Kathmandu, Nepal.

This research work presented here is genuine work done originally by me and has not been previously submitted, either in part or in its entirely, to any educational institution full in this or any other form to any university or institute, here or elsewhere, to confer a degree in any kind.

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ABSTRACT

Activated carbon (AC) has been successfully prepared from the chemical treatment of walnut shell (WS) powder. The carbonization temperature was 400°C for 3 hours in a tube furnace. Here, phosphoric acid was used as an activating agent in a 1:1 ratio by weight. Characterization was done by using Scanning Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FTIR), Methylene Blue and Iodine number, and electrochemical parameters like Cyclic Voltammetry (CV), Galvanostatic Charge- Discharge (GCD), Specific Capacitance, and Electrochemical impedance Spectroscopy (EIS). The SEM image showed a porous structure with some cracks present in it. The FTIR spectra clearly confirmed the oxygenated surface functional groups such as hydroxyl, carbonyl, carboxyl at the surface of prepared AC. Porosity was determined by Methylene Blue number and Iodine number so mesoporosity and microporosity was 181.66 mg/g and 787.40 mg/g respectively. The surface area was also determined by methylene blue adsorption method which was found to be 742.71 m^2/g. Electrochemical studies like CV, GCD and EIS were carried out to study application of prepared AC. The CV obtained was almost rectangular in shape displaying EDLC behavior.Similarly, GCD showed a specific capacitance of 145.5 F/g. Energy density was found to be 72.63 Wh/Kg and power density was found to be 900 W/Kg. The EIS result clearly showed a low resistance of 0.5 Ω. The results revealed that as laboratory prepared carbon material can be used as a potential material for electrode of supercapacitive devices.

Keywords: Capacitance, Charge discharge, walnut shell, chemically activated, EIS, porosity, Impedance, Electrochemical.

शोधसार

सक्रिय कार्वन (AC) एक ठूलो आन्तरिक सतह क्षेत्र र ठूलो छिद्र भएको एक अनाकार वस्तु हो । जस्का कारण यसमा इलेक्ट्रोकेमिकल गुणहरु र अवशोषण गुणहरु छन् , जुन तरल र ग्यास चरण अनुप्रयोगहरुको विस्तृत श्रृंखलामा प्रयोग गरिन्छ । यस कार्यमा , ओखरको बोक्रालाई रसायनिक रुपमा सक्रिय र परिमार्जन गरिएको थियो र उर्जा संकलनको लागि तिनिहरुको क्षमता अध्ययन गरिएको थियो । प्रयोगशालामा बनाइएको कार्वनको गुण जाँच्नको निम्ति स्क्यानिङ इलेक्ट्रोन माइक्रोस्कोपी (SEM), फोरियर ट्रान्सफर्म इन्फ्रारेड स्पेक्ट्रोस्कोपी (FTIR) , मिथिलिन ब्लू र आयोडिन नम्बर, र इलेक्ट्रोकेमिकल अध्ययनहरु जस्तै साइक्लिक भोल्टामेट्री (CV), ग्याल्भ्यानोस्ट्याटीक चार्ज डिस्चार्ज (GCD) र इलेक्ट्रोकेमिकल इम्पेडेन्स स्पेक्ट्रोस्कोपी (EIS) प्रयोग गरिएको थियो ।

वजनको 1:1 अनुपातमा फस्फोरिक एसिडलाई सक्रिय एजेन्टको रुपमा प्रयोग गरी ओखरको बोक्रा (WS) लाई 400°C मा तताएर सक्रिय कार्बन तयार गरियो । SEM ले यसमा रहेका साना प्वालहरु र चिराहरु देखाएको छ । FTIR ले तयार AC को सतहमा रहेका हाइड्रोक्सिल, कार्बोनिल, कार्बोक्सिल जस्ता अक्सिजनयुक्त सतह कार्यात्मक समूहहरु लाई स्पष्ट रुपमा पुष्टि गर्यो । पोरोसिटी मिथिलिन ब्लू र आयोडिन नम्बर बाट निर्धारण गरिएको थियो त्यसैले मेजोपोरोसिटी र माइक्रोपोरोसिटी क्रमश : 181.66mg/g र 787.40mg/g थियो । सतह क्षेत्र पनि मिथाइलिन ब्लू नम्बर बाट निर्धारण गरिएको थियो जुन 742.71m^2/g पाइयो । इलेक्ट्रोकेमिकल अध्ययनहरु गर्दा साइक्लिक भोल्टामेट्री (CV) , लगभग आयातकार थियो जसले EDLC व्यवहार देखाउँछ । ग्याल्भ्यानोस्ट्याटीक चार्ज डिस्चार्ज (GCD) ले 145.25 F/g को विशिष्ट क्षमता, उर्जा घनत्व 72.625 Wh/Kg र पावर घनत्व 900 W/Kg देखाएको थियो । इलेक्र्टोकेमिकल इम्पेडेन्स स्पेक्ट्रोस्कोपी (EIS) ले एकदम कम 0.5Ω प्रतिरोध देखायो । त्यसैले प्रयोगशालामा बनाएको कार्बन सुपरकापासिटिभ मेसिनमा प्रयोग हुने इलेक्ट्रोड मटेरिएलको रुपमा प्रयोग गर्न सकिने निष्कर्ष निस्कियो ।

LIST OF ABBREVIATIONS

AC: Activated carbon

MB: Methylene blue

ppm: Parts per million

rpm: Rotation per minute

I_N: Iodine adsorption number

MB_N: Methylene blue number

FTIR: Fourier Transform Infrared Spectroscopic analysis

FE-SEM: Field-Emission Scanning Electron Microscopy

CV: Cyclic Voltammetry

GCD: Galvanostatic Charge- Discharge

EIS: Electrochemical Impedance Spectroscopy

WS-1: As prepared activated carbon

WS-2: Acid treated sample

WS-3: Raw sample

CS: Commercial sample

WSP: Walnut shell powder

g: Gram

nm: Nanometer

µm: Micrometer

hrs: Hours

s: Second

A/g: Ampere per gram

F/g: Faraday per gram

W/Kg: Watt per kilogram

Wh/Kg: Watt hour per kilogram

m^2/g: Meter square per gram

mg/g: Milligram per gram

mg/L : Milligram per litre

mV : Millivolt

C_{sp}: Specific capacitance

E: Energy density

P: Power density

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CHAPTER I

1. INTRODUCTION

1.1 General introduction

Activated carbon (AC) refers to carbon-based materials with high surface area, porous structure, and diverse oxygenated functional groups. Lignocellulosic resources and waste biomass have gained significant interest in recent years due to their physicochemical characteristics, carbon adsorption properties, micro-nanostructure, and potential applications (González-García, 2018). Bio-based AC synthesis has gained attention for green and sustainability projects. Woody biomass, agro-wastes, and industrial non-feed crops like hemp and jute are used to manufacture promising ACs. Despite being often used for water purification, there is limited use of activated carbon in electrochemical storage devices. Natural biomasses, similar to commercial energy crops, are ideal precursor materials for Supercapacitor (SC) electrodes.(Mandal et al., 2023) Activated carbon is a highly porous material that is advantageous for sorption and catalytic applications because it has hydrophilic surface functional groups and a hydrophobic graphene layer.

Carbon materials find widespread application due to their numerous applications, diverse synthesis techniques, abundant supplies, and large surface area, as well as their tunable heteroatom doping, pore size distribution, and superior conductivity. The performance in a typical application will be significantly impacted by these special qualities of carbon materials. For instance, mesoporous carbon tends to be chosen over micro porous carbon when employed as an electrode material for batteries, which results in the mass transfer limitation. (Liu et al., 2021)

Activated carbons, prepared from bio waste, have been synthesized successfully, offering environmental friendliness, low cost, and renewability. These bio waste alternatives are considered a positive alternative to conventional raw materials like petroleum coke, tar pitches, and coal. Numerous studies have explored activated carbon from various bio waste sources. (Cheng et al., 2020) Many sources of lignocellulose biomass, including durian, coconut, rubberseed, hazelnut, palm kernel, almond, plum stones, cotton stalks, rice husk, pistachio-nut, walnut, and wood, can be used to create activated carbon with a high adsorption capability. For the elimination

of pollutants, activated carbon made from lignocellulosic biomass is extensively utilized. Lignocellulosic activated carbon is used in many different industrial sectors for tasks like air pollution control, wastewater treatment, chemical reactions, adsorption of volatile organic compounds (VOCs) (Mohamad Nor et al., 2013) and as technological platform for electrochemical storage. (Raza et al., 2018)

After fruit processing at walnut kernel manufacturing facilities, a large volume of walnut shell is accessible; however, only a small percentage has been utilized in industry. In actuality, the majority of it is burned for fuel or thrown away as waste. However, this has no utility benefit and pollutes the environment. Thus, it's imperative to discover better, alternative uses for walnut shells. Since cellulose, hemicellulose, and lignin make up the majority of the shell, the composition of walnut shells is fairly comparable to that of other wood biomass.(Jahanban-Esfahlan et al., 2019) Walnut shells comprise a high surface area, minimal ash content, and exceptional chemical stability. (Albatrni et al., 2022)

Activated carbons (ACs) derived from walnut shells offer a sustainable and cost-effective solution for various applications, particularly in electrochemical energy storage. The activation temperature significantly influences the porosity development, with higher temperatures leading to increased surface area and pore volume**.** (Pavlenko et al., 2018). Activated carbon can also be referred to as solid sponge, activated charcoal, or activated coal. Activated carbon can be divided into a number of categories according to its physical characteristics, including extracted activated carbon (EAC), granulated activated carbon (GAC), powdered activated carbon (PAC), and extracted activated carbon (PAC) .(Yahya et al., 2015)

From the perspective of social sustainability and environmental friendliness, porous carbon materials are becoming more and more attractive for use as electrode materials in supercapacitors and lithium-sulfur cells, as well as hydrogen storage adsorbents, due to their availability, adjustable microstructure, variety of forms, and large specific surface area. As a result, a lot of work has gone into creating and customizing the microstructures of materials formed of porous carbon using different activation techniques (such as chemical and physical activation). (Wang and Kaskel, 2012)

Electrochemical capacitors, often known as supercapacitors (Gamby et al., 2001) are electrochemical energy storage devices with high electrochemical capacitance

performance. Supercapactors store energy by ion adsorption or rapid surface redox reactions. They can be used instead of batteries to store and harvest electrical energy. Recent advances in charge storage methods and nanostructured materials have resulted in higher performance. Higher capacitance for electrochemical double layer capacitors utilizing carbon electrodes with subnanometer holes has been achieved. Combining pseudo-capacitive nanomaterial with nanostructured lithium electrodes has increased the energy density of electrochemical capacitors to match that of batteries. Mathematical modeling and simulation are critical for developing high-energy, high-power devices.(Simon P et al., 2008)

Pseudocapacitors and Electrochemical Double Layer Capacitors (EDLCs) are the two forms of supercapacitors. Although conducting polymer-based electrodes or metal oxide surfaces undergo redox reactions to produce high specific capacitance, pseudocapacitors' low energy density, short cycle life, low electrical conductivity, and high cost prohibit their practical use in portable electronic devices. Through the formation of an electric double layer between the electrode and electrolyte that has appropriate stability and rate capability, EDLCs are able to store electricity. Thus, it has been demonstrated that the electrode materials have a big impact on how well SCs work. Therefore, the creation of highly effective electrode materials with increased surface area is imperative for improving the SC devices' performance. (Elanthamilan et al., 2021)

The development of electrical double layer capacitors (EDLCs), or so-called supercapacitors of high specific performance, makes the study and modeling of the physical (gas phase) as well as the electrochemical characteristics of nanoporous carbon in non-aqueous electrolytes very important. EDLCs are very quickly rechargeable and can deliver tremendous power in a matter of seconds. The high power density, high electrical efficiency, reversibility, low temperature coefficient for energy and power densities, and excellent cyclability of EDLCs make them valuable in power electronic systems as well as other highly promising systems in a variety of contemporary technology domains, including computer, automotive, and space**.** (Jänes et al., 2007)

Together with lithium ion secondary batteries, supercapacitors can be utilized as an additional power source in hybrid electric automobiles. Highly developed porous

carbon materials, such as activated carbon, carbon nanofibers, and mesoporous carbons, are typically used as the electrode materials for supercapacitors. (Lee et al., 2014)

Two carbon electrodes and a liquid electrolyte supported in a porous matrix (separator) positioned between the electrodes make up a conventional supercapacitor. A carbon-based supercapacitor's capacity to store energy is primarily determined by its electrodes' specific surface area and pore structure, ionic conductivity, and electrolyte voltage stability. Consequently, common components of conventional electrodes, such as carbon fibers, carbon aerogels, and activated carbons, need to have a large surface area. Aqueous solutions of H_2SO_4 or KOH or non-aqueous solutions of tetraethyl-ammonium tetrafluoroborate in organic solvents are the electrolytes typically employed in supercapacitors. Supercapacitors employ solid polymer electrolytes as an alternative to liquid electrolytes, and this development may have a number of benefits. From a technological perspective, there are advantages in terms of easier packaging, a more compact shape, and a more flexible construction. A safer gadget free of hazardous and caustic liquid leaks is also advantageous from a management perspective. (Lufrano and Staiti, 2010)

The majority of renewable energy sources, with the exception of biofuels, are supplied as electricity. A dependable technological platform for electrochemical storage, such as batteries, fuel cells, and electrochemical supercapacitors (SCs), has thus been in high demand. Specifically, quick storage capacity (i.e., short discharge time: SC: 1–10 s vs. lithium-ion battery: 10–60 min) and improved cyclic stability (SC > 30,000 h vs. battery > 500 h) have attracted greater attention to SCs than batteries. Apart from their poor energy density, new developments in SCs concerning electrode materials and electrolytes have great promise to bridge the gap between current electrolytic-capacitor technology and that of batteries and fuel cells. (Raza et al., 2018)

1.2 Synthesis and activation of activated carbon (AC)

In order to synthesize activated carbon, carbonaceous raw materials are generally washed, dried, crushed into fine powder and sieved to appropriate particle size. Then it is pyrolysed or carbonized by controlling different parameters like temperature,

heating rate, holding time, inert environment etc. Carbon is activated using chemical or by subjected to proper activation process in order to enhance pore size and volume.

Activation means the process that is employed to increase surface area and porosity from a carbonized organic precursor and the resulting broad group of materials is referred to as AC. Organic precursor usually have a relatively low porosity and their structure consists of elementary crystallites with a large number of interstices between them.

Although the synthesis of carbon materials with an organized porous structure in the mesoporous region is very desirable, practical applications necessitate the inclusion of microporosity, which is commonly found in activated carbon. The micropores serve as the adsorptive molecule's adsorption sites, while the mesopores serve as diffusion channels to the inner porosity. Thus, the development of carbon materials with regulated micro- and mesoporosity is of essential relevance in order to achieve high adsorption capacity as well as quick adsorption kinetics for processes involving big molecules**.** (Juárez-Galán et al., 2009)

1.3 Application of Activated Carbon (AC)

AC possesses a wide array of applications across environmental, industrial and energy sectors, owing to its remarkable adsorption properties. According to a study by (Zhao et. al., 2019), AC is extensively utilized for the removal of pollutants such as dyes, heavy metal and pesticides from air and water sources, thus contributing to environmental remediation efforts. Furthermore, AC is employed in various industries, including food, pharmaceuticals, chemicals, oil and mining for water treatment processes (Zhao et al., 2019). Additionally, AC plays a crucial role in energy related fields, where it is utilized in batteries, solar cells, sensors and supercapacitors, therby contributing to advancements in renewable energy technologies. (Lu et al., 2020)

Supercapacitors, one of the most significant and promising environmental technologies that will have a major impact on raising the standard of living and capabilities of our civilization in energy storage. In particular, electrochemical capacitors are quick to charge and discharge and have extended lifespans as effective energy storage units. As a result, capacitor technology is thought to be a potential method of storing energy. Using this technology in conjunction with renewable

energy sources has the added benefit of boosting effectiveness. Electrochemical capacitors have been the subject of intense research in an effort to increase their energy density in recent years. However, due to their relatively low energy densities, electrochemical capacitors have restricted applications and are unable to completely satisfy the performance requirements of the electrical equipment that is now in use. In order to maximize energy and power densities, future energy storage technologies for cars and smart grids must have both the high energy density capabilities of lithium ion batteries and the quick charge/discharge rates of electrochemical capacitors. (Naoi et al., 2013)

In recent years, hybrid electric vehicles and mobile devices have become popular. For these devices, scientists have felt that an energy storage system having high energy density and excellent rate performance was needed. Supercapacitor (SC) is the class of efficient energy storage devices which have attracted the attention of scientists since they possess high power and high energy density, long lifetime cycle, and excellent charge discharge rates. On the basis of charge storage mechanism, SC is basically classified into two types: Pseudo capacitor and Electric double layer capacitor (EDLC). Pseudo-capacitor (PC) shows a faradic process that means fast and reversible redox process at the electroactive material surface whereas EDLC exhibits a non-faradic reaction involving electrode-electrolyte interface. The energy storage mechanism in supercapacitor is similar to that of capacitor can be described as follows:

A capacitor is a component of an electrical circuit made up of two metal sheets that are spaced apart by a dielectric substance. Its behavior is governed by the equation (1)

$$C=\frac{q}{V} \dots \dots \dots \dots (1)$$

Where, q is the charge stored in capacitor (in coulombs, C)

V is the potential across the capacitor (in volts, V)

C is the capacitance (in farads, F)

A capacitor's metal plates will accumulate charge when a voltage is put across them until q satisfies equation (1). During this charging process, a current called charging current will flow as a consequence an excess of electrons on one plate and a deficiency of electrons on the other occurs.

1.4 Characterization of Activated Carbon

1.4.1 Scanning Electron Microscopy (SEM)

A type of electron microscopy called scanning electron microscopy (SEM) creates images of samples by scanning a rectangular region of the material with a focused electron beam. When the electron beam interacts with sample, it loses energy by a variety of mechanisms. The lost energy is converted into alternative forms such as heat, emission of low energy secondary electrons and high-energy backscattered electrons, light emission or X-ray emission, all of which provide signals carrying information about the properties of the sample surface such as its topography and composition. (Mohammed et al., 2018)

In this study, SEM was used to study the surface texture and the nature of the surface of AC. The presence of macro and mesopores on the surface of AC can be seen in high magnification SEM images.

1.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is one of the useful techniques to determine the various surface functional groups present in the sample (Blando et al., 2001). In this technique, spectrums are observed after absorption of IR wavelengths. Analysis of these observation spectra reveals the functional groups present in the sample. When the frequency of IR same as vibrational frequency of a bond, then absorption occurs. Only IR active compound gives the spectra.

1.4.3 Electrochemical Characterization

a) Cyclic Voltammetry

Cyclic voltammetry (CV) is a potentiodynamic electrochemical measurement. A triangle voltage waveform is used to stimulate the current response of a tiny stationary in an unstirred solution in CV. The potential varies linearly with respect to the reference electrode. When the potential reaches its limit, the scan direction is reversed and the potential is reset to its original value. The excitation cycle is frequently repeated multiple times. The voltage extrema at which reversal happens are referred to as switching potentials. For a specific experiment, a diffusion-controlled oxidation or reduction of one or more analytes is performed. The direction of the initial scan may be negative or positive depending on the sample makeup. A scan in the opposite

direction is referred to as reverse scan. Cycle periods typically range between 1ms and 100s. The resultant current at the working electrode is plotted against the applied voltage to create a cyclic voltammogram.

b) Chronopotentiometry

The technique involves measurements and interpretation of potential- time curves and was earlier known as constant current voltammetry. In chronopotentiometry, a small current is flown through a cell containing a working and an auxillary electrode. The potential changes of the working electrode are monitored against another reference electrode. The cell also contains enough supporting electrolyte to ensure that the electro-active species is transported by diffusion only. The potential changes of the working electrode are plotted against time, and the resulting chronopotentiogram has analytical applications and is also useful for investigating electrode kinetics. Here, it is used for calculating specific capacitance. The specific capacitance(C_{sp}), energy density and power density is given by,

$$C_{sp} = \frac{\mathbf{I\Delta t}}{m\Delta V} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$E = \frac{1}{2} \times C_{sp} (\Delta V)^2 \ldots\ldots\ldots\ldots (3)$$

$$P = \frac{E}{\Delta t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where,

I: Constant current in A

Δt: Discharge time in s

m: Mass of activated carbon

ΔV : Potential window

E: Energy density

C_{sp}: Specific capacitance

P : Power density

c) Electrochemical Impedance Spectroscopy (EIS)

The examination of electrochemical impedance spectroscopy, or EIS, is a crucial analytical method for learning more about the capacitive events that occur in the electrodes and the distinctive frequency response of supercapacitors.

Electrochemical Impedance Spectroscopy (EIS) is a strong electrochemical technique for determining the electrical characteristics of electrochemical systems. (Chen et al., 2003) EIS involves applying a small amplitude sinusoidal voltage or current signal to a system over a range of frequencies and measuring the impedance response that results. EIS is widely used to study corrosion, batteries, fuel cells, sensors, and other electrochemical processes because it provides useful information about the electrical behavior of electrochemical interfaces, such as solution resistance, charge transfer resistance, and double-layer capacitance.

1.4.4 Determination of Porosity

Porosity of activated carbon can be determined by adsorption studies. Here methylene blue and iodine is used as model chemical substances:

a) Methylene blue number (MB_N)

Methylene blue number is the amount of methylene blue dye absorbed by one gram of dried activated carbon. It measures the mesopore content of activated carbon.The amount of methylene blue adsorbed from each was calculated by using equation,

$$C_e = \frac{\text{Absorbance}}{\text{Slope}} \quad \ldots\ldots\ldots\ldots\ldots (5)$$

$$MB_N = \frac{C_o - C_e}{M} \times V \quad \ldots\ldots\ldots\ldots\ldots (6)$$

Where,

C_o: Initial concentration of MB (in mg/L)

C_e: Final concentration of methylene blue solution (in mg/L)

M: Amount of the adsorbent taken (in gram)

V: Volume of solution taken (in liter) (Raposo et al., 2009)

Methylene blue is a synthetic cationic thiazine dye of an amorphous nature with a molecular formula $C_{16}H_{18}ClN_3S$. It is also called basic blue 9, tetramethylthionine

chloride. It is dark green powder, with a characteristic deep blue color in aqueous solution where it dissociates into an MB cation $[C_{16}H_{18}N_3S]^+$ and a chloride anion $[Cl]^-$. Methylene blue is commonly use to probe the mesopores volume of activated carbon by adsorption method.

Surface area of adsorbent is generally done by Methylene blue adsorption method using,

$$S_{MB}=\left(\frac{Q_m a_{MB}.N}{M}\right) \text{.....(7)}$$

Where,

S_{MB}: Surface Area

Q_m: Maximum Loading

a_{MB}: Cross Sectional Area of methylene blue

N: Avogadro's Number

M: Molecular Weight of MB

b) Iodine Number

Iodine number is commonly used parameter for determination of surface area and porosity of activated carbon. Iodine number is the milligrams of iodine adsorbed by 1g of activated carbon from a 0.1N iodine solution when the equilibrium iodine is exactly 0.02N. As the size of iodine is similar to that of micropore range so it indicates the concentration of micropores in the AC. Iodine number measures micro-pore content of the activated carbon. A higher iodine number indicates higher microporosity of the sample. It is a measure of the micropore content of the activated carbon (0-20 A, or upto 2nm) by adsorption of iodine from solution. Adsorbents with a high iodine number often have a large surface area and work well for adsorbing tiny molecules.(Bestani et al., 2008) (Ratan et al., 2018)

Iodine number of activated carbon varies with the factors such as, precursor materials, carbonization process, temperature, activating reagent, pore volume distribution, presence of adsorbed volatiles, etc.

The determination of iodine number is based on the fact that the unused or reactivated carbons can adsorb the iodine from aqueous solution. The fundamental reaction of iodine and unsaturated carbon can be depicted as follows:

$$H_2C = CH_2 + I_2 \rightarrow H_2IC - CH_2I$$

The calculation of iodine number can be done by using the formula,

$$\text{Iodine number } (I_N) = \frac{\text{Amount of iodine (mg) adsorbed by carbon}}{\text{Weight of carbon taken in g}} \ldots\ldots\ldots\ldots (8)$$

1.4.5 Adsorption isotherm

While doing experiment on adsorption it is necessary to use some adsorption isotherms for the calculation of affinity of adsorbent and adsorbate, maximum absorption capacity (mg/g) of the adsorbent and heterogeneity of adsorbent, etc. Following are some isotherm models which can be used in calculating different factors used in adsorption. (Ratan et al., 2018)

Langmuir adsorption isotherm characterizes the affinity of adsorbent and adsorbate, and maximum absorption capacity (mg/g) of the adsorbent. The equation of Langmuir adsorption isotherm can be linearized as;

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \ldots\ldots\ldots\ldots\ldots (9)$$

Where,

$\mathbf{Q_e}$: Equilibrium concentration of adsorbate

$\mathbf{C_e}$: Equilibrium concentration of adsorbent

$\mathbf{K_L}$: Langmuir constant (Ratan et al., 2018)

CHAPTER II

2 LITERATURE REVIEW

2.1 Literature review

Various types of activated carbons were tested from the PICA Company in supercapacitor cells in order to compare their performances. The changes measured in specific capacitance and cell resistance have been shown. The PICACTIF SC carbon was found to be an interesting active material for supercapacitors, with a specific capacitance as high as 125 F/g. (Gamby et al., 2001)

Application of high surface area activated carbon (AC) derived from rice husks were reported to prepare AC free from Bronsted and Lewis acid sites and electrical double layer capacitance as the main charge storage mechanism. The sample that exhibited the highest specific capacitance (147 F g^{-1}) was synthesized at an activation temperature of 850 °C and had a surface area of 2696 m^2 g^{-1}. In-depth impedance analyses showed that this activated carbon sample had a low resistance (0.23 Ω) and the supercapacitor electrode had a quick frequency response of 0.11 s, according to detailed impedance testing. (Teo et al., 2016)

Study was done emphasing the effectiveness of combining conventional activated carbon nanomaterials to develop high- performance nanocomposite electrodes for supercapacitors. The optimization of electrode composition and the utilization of commercially available materials are consistent strategies across these studies, highlighting the potential for industrial- scale production of advanced supercapacitor electrodes. (Cheng et al., 2020)

Walnut shell- derived activated carbon for benzene removal in gas sweetening system was explored. It follows the chemical activation method using $ZnCl_2$ and H_3PO_4. Operating parameters are optimized via the Taguchi method. Results show H_3PO_4 activation yields higher surface area (1544 m^2/g), while $ZnCl_2$ activation enhances benzene removal (69.22 mg/g). Benzene uptake increases with concentration and contact time. The study contributes to understanding the potential of walnut shell-derived activated carbon for gas purification applications (Mataji & Khoshandam, 2014)

Walnut shell- based porous carbon obtained through carbonization, hydrothermal and activation treatment, showcasing superior electrochemical performance for supercapacitors was presented. The porous carbon exhibits a remarkable specific capacitance of upto 462 Fg^{-1} at Ag^{-1}, along with excellent cycling stability (94.2% capacitance retention after 5000 cycles at 10 Ag^{-1}). Additionally, a symmetric supercapacitor utilizing this material achieves high specific capacitance (197Fg^{-1} at 1 Ag^{-1}), considerable cycling stability (89.2% capacitance retention after 5000 cycles at 5 Ag^{-1}), and impressive power/energy density (42.8 Wh/kg at 1249 WH/kg). This synthesis approach and the electrochemical performance highlight the walnut shell derived porous carbon as a promising electrode material for supercapacitors. (Wang et al., 2019)

(Liu et al., 2020) used corn cob to make activated carbon. Corn cob was activated with potassium hydroxide. Analysis techniques such as SEM, BET, Raman, FTIR, and XPS were utilized to describe the physical and chemical characteristics of activated carbon. On the mercury ion removal rate, the effects of adsorbent dosage, adsorption period, pH, and initial Hg(II) concentration were investigated.

(Kuang et al., 2020) examined the ability of surfactant-modified activated carbon to remove MB from aqueous solution. The study's objectives were to use adsorption models to confirm the adsorption rate and capacity; to identify the various factors, such as initial dye concentration, temperature, pH, adsorbent dose, and additive salts, that influence sorption; and to measure the adsorption effect of adsorbent in actual water samples.

Investigation was done on commercial activated carbon (CAC) and locally manufactured activated carbons made from bamboo dust, coconut shell, groundnut shell, rice husk, and straw, the kinetics and mechanism of methylene blue adsorption. Using a batch adsorption technique, the impacts of different experimental settings have been studied to learn more about how to handle dye industrial effluents. First order kinetic equations and the Freundlich and Langmuir adsorption isotherms were used to model the adsorption data. The adsorption abilities of locally produced activated carbons and commercial activated carbon have been examined. According to the findings, these carbons could be used as low-cost substitutes for commercial

activated carbon in wastewater treatment to remove dyes and colors. (Kannan and Sundaram, 2001)

(Mahmud et al., 2021) pyrolyzed pineapple waste biomass (PWB) to create suitable adsorbents like biochar(BC) and activated carbon(AC) to remove MB from water. Prior to use, the surface area, functional groups, and surface morphology of AC-PWB and BC-PWB were characterized. The investigation of MB removal involved changing the initial MB concentration, contact time, adsorbent dosage, and temperature. The outcomes indicated that AC-PWB had a greater ability for adsorption than BC-PWB. Overall study concluded, PWB can be used as a valuable raw material to create affordable and ecologically friendly adsorbent to remove dye from solution.

(Bardhan et al., 2020) prepared betel nut husks derived activated carbon (BNH-AC) for the first time using sodium hydroxide (NaOH) activation with a 1:3 NaOH impregnation ratio. C=O and C-H were identified as active functional groups in the reaction of cationic methylene blue (MB) dye by FTIR analysis of BNH-AC. The Freundlich isotherm model and pseudo-second-order kinetics were used in the adsorption of MB. As a result, the BNH-AC is a promising and cost-effective adsorbent for MB dye treatment, with a high adsorption capability.

(Joshi & K.C., 2020) made a variety of activated carbons (ACs) from sugarcane bagasse powder by impregnating it with $ZnCl_2$ at different weight ratios of 0.25:1, 0.5:1, 1:1, and 2:1. The iodine number, methylene blue number, surface area, scanning electron microscopy (SEM), and x-ray diffraction were used to analyze the characteristics of the activated carbons (ACs).The AC created at a $ZnCl_2$ to sugarcane bagasse impregnation ratio of 1:1 produced the highest value of iodine number (868 mg/g). SEM micrographs of AC-1's surface reveal the existence of well-developed pores. All of the ACs are amorphous materials, according to the large peaks in the XRD patterns. Conclusion: The $ZnCl_2$ impregnation concentration is beneficial in promoting surface area and porosity growth in the AC made from sugarcane bagasse.

(Joshi & Pokharel, 2014) activated Lapsi seed stone chemically with potassium hydroxide at 400°C to produce activated carbon (AC). The pH, moisture content, FTIR spectroscopy, scanning electron microscopy (SEM), methylene blue (MB), and iodine number were used to describe the AC. FTIR spectra showed that the surface of

AC had a variety of functional groups that contained oxygen. SEM pictures demonstrate the very porous and cavity-filled nature of AC. The AC's Iodine number indicated that it was extremely microporous. The Langmuir and Freundlich adsorption isotherms were used to examine the methylene blue adsorption by produced AC. The investigation demonstrated that the potassium hydroxide-activated Lapsi seed stone AC could be a low-cost adsorbent with advantageous surface characteristics.

In a study, ACs activated at 400 °C and post-treated at 800 °C exhibited exceptional electrochemical performance, demonstrating a high capacitance of 123 Fg^{-1} per mass of one electrode and stable cycling performance over 5000 cycles. These findings underscore the potential of walnut shell-derived ACs for high-performance energy storage applications.(Pavlenko et al., 2018)

Walnut shells were used as the carbon source, and $KMnO_4$ was used as the activator and template agent to create a hybrid process that produced hierarchical porous carbons. The materials made of hierarchical porous carbon have a high capacitance of 380 F g^{-1} at 0.5 A g^{-1}, as well as good cycling stability, with 93% of the capacitance remaining after 10,000 continuous cycles of charge and discharge at 5 A g^{-1}. Furthermore, with an energy density of 8.95 Wh kg^{-1}, the built symmetric supercapacitor exhibits outstanding performance. According to this work, high performance carbon electrode materials for supercapacitors may be prepared gently and extremely effectively using $KMnO_4$ activation. (Zhang et al., 2023)

Similarly, another study using walnut shells produced activated carbon that was employed as an electrode material for supercapacitors at 600, 700, and 800 °C. The capacitive properties were predicted using galvanostatic charge-discharge tests, electrochemical impedance analysis, and cyclic voltammetry. The Wn-800 sample had a greater specific capacitance value (595 F/g at a current density of 1 A/g) than the other samples because of its superior morphological feature. At a current density of 3 A/g, the Wn-800@Ni electrode additionally demonstrated 91% of its capacitance retention value up to 6000 GCD cycles. Thus, it was determined that porous AC samples made from walnut shells would make excellent electrode materials for energy storage devices. (Elanthamilan et al., 2021)

By activating KCl templated biochar with CO_2 at 900°C, large specific surface area (1958 m^2 g^{-1}) activated carbon (AC) was produced. Electrochemical impedance

spectroscopy, galvanostatic charge/discharge, and cyclic voltammetry were used to assess the electrochemical properties. The inner resistance of WS-90 had a comparatively low 1.7 Ω. With a capacitance retention ratio of 95.4%, the specific capacitance in 6 mol L^{-1} KOH electrolyte at a current density of 0.1 A g^{-1} was 245.0 F $g^{-1}$and could withstand 4000 cycles (0.1, 0.5, 1.0, and 5.0 A g^{-1} for 1000 cycles, respectively) with a specific capacitance of 245.0 F g^{-1} at current density of 0.1 A g^{-1}. (Cao et al., 2016)

CHAPTER III

3 OBJECTIVES

3.1 General Objective

General objective of the study is to prepare and characterize activated carbon prepared from agricultural waste byproduct i.e. walnut shell. Then, as prepared material has been used as a material for energy harvesting and storage.

3.2 Specific Objectives

i. To prepare highly porous activated carbon from locally available ecofriendly material walnut shell by carbonization technique.
ii. To activate the material chemically using phosphoric acid for the development of porosity by mixing walnut shell powder and phosphoric acid.
iii. To characterize activated carbon using various techniques as SEM, FTIR, iodine number and methylene blue number.
iv. To study the electrochemical properties of as prepared activated carbon using Cyclic Voltametry (CV), Galvanostatic charge discharge (GCD) and Electrochemical impedance spectroscopy (EIS).

CHAPTER IV

4 MATERIALS AND METHODS

4.1 Instruments

Following instruments have been utilized in entire research work

a) **Herbal Grinder**

Grinder was used to grind the Walnut Shell.

b) **Sieve**

Sieve of 250μm pore size was used to sieve the sample grinded in grinder.

c) **Electronic balance**

Phoenix, PH2204C, was used to weigh out the sample.

d) **Hot air oven**

Materials were dried and preheated in Eurolab hot air oven.

e) **Tube Furnace**

KJ-T1200,AC220V single phase,50Hz, max power 2kW, Serial no. KJLXR21120704, of ZHENGZHOU KEJIA FURNANCE CO., LTD was used for the preparation of activated carbon.

f) **Scanning Electron Microscopy (SEM)**

To study the surface morphology of the carbonized sample ZEISS, Scanning Electron Microscope, Germany was used.

g) **Sonicator**

DC-150H of mrc laboratory equipment was used for dispersion of slurry equally in nickel foam sonicator.

h) **Rotatory Flask Shaker**

For adsorption of sample Rotatory Flask Shaker was used.

i) **Filter Paper**

Whatman-1, 125μm, was used to filter.

j) **Mortar and Pestle**

COLE-PARMER INSTRUMENT 04010-00 was used for grinding the carbon into smaller particles.

k) Fourier Transform Infrared Spectroscopy (FTIR)

Surface functional groups of the carbon samples were studied by using PerkinElmer 10.6.2, FTIR spectrophotometer.

l) Cyclic Voltammetry and Chronopotentiometry

Electrochemical workstation CS350H, CORRTEST (Wuhan, China) has been used for cyclic voltammetry and chronopotentiometry measurements in order to investigate the electrochemical properties of the carbon sample.

m) Counter Electrode

Platinum wire was used as counter electrode.

n) Reference Electrode

Hg/HgO electrode was used as reference electrode.

4.2 Chemicals

i. **Phosphoric acid**: Ortho Phosphoric acid (H_3PO_4 88%) from Fisher Scientific was used for activating the precursor.

ii. **Potassium dichromate solution**: Potassium dichromate was obtained from SD Fine and solution was used to standardize sodium thiosulphate solution.

iii. **Sodium thiosulphate**: Sodium thiosulphate was obtained from SD Fine and solution. It was used to standardize Iodine solution for calculation of Iodine Number.

iv. **Hydrochloric acid (LR)**: The (35%) Hydrochloric acid was used from LOBA CHEMIE PVT. LTD.

v. **Sodium bicarbonate**: Sodium bicarbonate was purchased from Fisher Scientific, India.

vi. **Iodine**: Iodine was used from the Fisher Scientific, India.

vii. **Potassium Iodide**: EMPLURA Potassium Iodide was used.

viii. **Starch**: Starch solution was used as indicator which is obtained from Qualikems.

ix. **Charcoal Activated** - 250: The Qualigens activated Charcoal was used.

x. **Ethanol** (AR): Absolute ethanol was used for dispersion of sample.

xi. **Methylene Blue:** Methylene blue of Merck company was used.

4.3 Preparation of Activated Carbon

4.3.1 Preparation of Walnut Shell Powder (WSP)

Walnut Shells were collected from local market of Kathmandu. Inner part of walnut was removed and walnut shells were washed and dried in sunlight. **Figure 1** shows the walnut shells.

Figure 1 : Walnut Shells

The material was then grinded into fine powder in an electric grinder and sieved through 250μm sieve. Sieved materials were preheated for 2 hrs in hot air oven at 200 °C for moisture removal. Then, precursor was treated with phosphoric acid (H_3PO_4) in 1:1 ratio by weight and was left for 24 hrs at room temperature. It was again heated in an oven at 110 °C for 2 hrs. Subsequently, the prepared material was carbonized in a tube furnace at 400 °C for 3hrs by applying inert nitrogen atmosphere in tube furnace. After that, prepared activated carbon was washed with hot distilled water till neutral pH was obtained. Again, it was dried at 110 °C in hot air oven. Finally, it was grinded into fine powder using Mortar and Pestle to obtain fine powder of activated carbon. Thus obtained AC was shown in **Figure 2**.

Figure 2: As Prepared AC from Walnut Shell

The overall experimental processes are shown in flow chart diagram **Figure 3:**

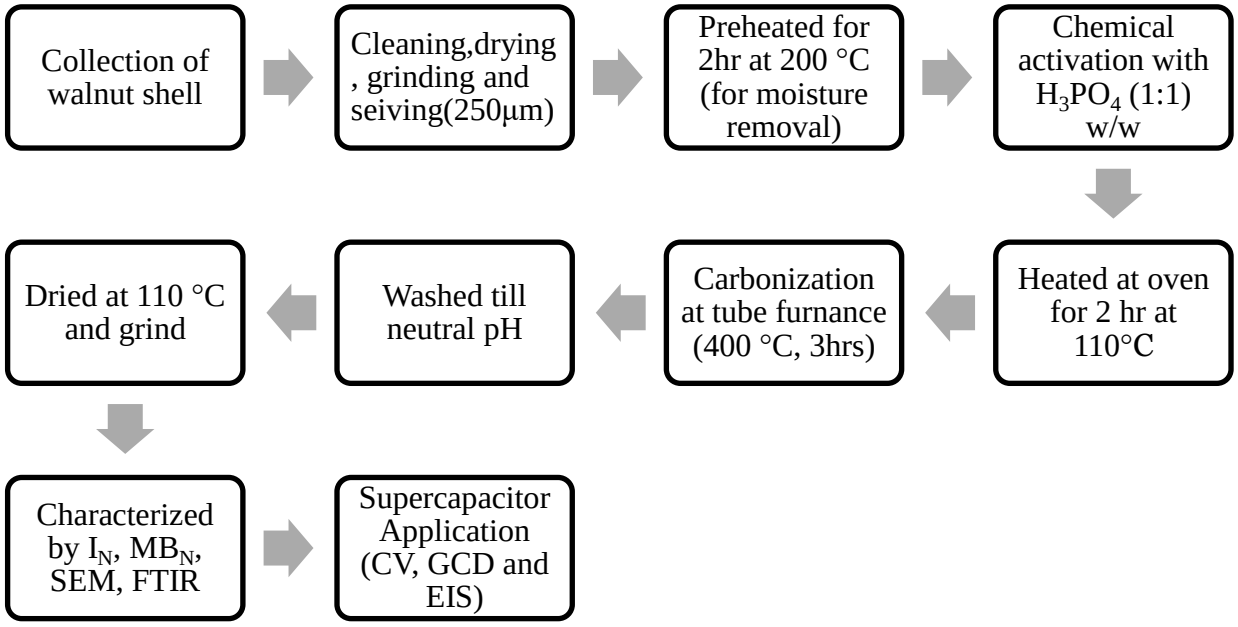

Figure 3: Flowchart diagram for overall process of experiments

4.3.2 Preparation of carbon samples

a) Raw precursor (WS-3)

Walnut Shells were washed and dried in sunlight. The material was then grinded into fine powder in an electric grinder and sieved through 250 μm sieve. Sieved materials were preheated for 2 hrs in hot air oven to remove moisture.

b) Acid treated carbon (WS-2)

Walnut Shells were washed and dried in sunlight. The material was then grinded into fine powder in an electric grinder and sieved through 250μm sieve. Sieved materials were preheated for 2 hrs in hot air oven at 200°C for moisture removal. Then, precursor was treated with phosphoric acid (H_3PO_4) in 1:1 ratio by weight and was left for 24 hours at room temperature.

c) Carbonization of Sample (WS-1)

Acid treated sample was placed in a ceramic combustion boat and was inserted inside the tube furnace. Then, the temperature of tube furnace was increased at the rate of 5°C per minute. It was carbonized at 400°C for 3 hrs in an inert nitrogen atmosphere.

Inert atmosphere was created by a continuous flow of pure nitrogen. The carbonized sample was then cooled to room temperature.

Table 1: Table showing sample name and condition maintained during preparation of samples

Sample	Particle size (µm)	Preheating temperature prior to activation (°C)	Preheating time (hr)	H_3PO_4 : WSP ratio (wt:wt)	Heating temperature after chemical treatment (°C)	Heating time after chemical treatment (hr)	Carbonization temperature (°C)	Carbonization time (hr)
WS-3	<250	200	2	-	-	-	-	-
WS-2	<250	200	2	1:1	110	2	-	-
WS-1	<250	200	2	1:1	110	2	400	3

4.4 Characterization

The porosity developed in the AC was determined by using the methylene blue number and iodine number. The surface area was determined by using the methylene blue adsorption method. The functionality of the activated carbon was obtained by FTIR spectroscopy method, SEM was used to determine surface morphology of AC, and CV, GCD and EIS for electrochemical characterization.

4.4.1 Scanning Electron Microscopy (SEM)

The surface morphology of the as prepared walnut shell based activated carbon was studied with scanning electron microscopy at an accelerating voltage of 3.00kV. For SEM observation. In this study, ZEISS SEM was used.

4.4.2 Fourier Transmission Infrared (FTIR) Spectroscopy

FTIR spectra of the samples were recorded using Perkin Elmer Spectrometer 10.6.2 version. All the spectral data were obtained at wave number of 4000-500 cm^{-1}.

4.4.3 Electrochemical characterization of the carbon materials

Electrochemical measurements were performed in a three-electrode cell, in which as prepared activated carbon sample was used as the working electrode, Platinum (Pt) wire electrode as a counter electrode, Hg/HgO as reference electrode and KOH (1M)

as an electrolyte. The working electrode was fabricated in laboratory by using carbon sample, PVDF (binder) and commercial activated carbon in a 8:1:1 ratio and was grinded in a mortar and pestle with dropwise addition of isopropyl alcohol. It was then transferred to clean vile and sonicated for 15 minutes. Then, pure Ni foam was taken and its weight was measured. The sonicated solution was applied to Ni foam by drop casting method. It was then dried in oven at 60 °C for 10 minutes. The process was repeated until the solution was completely applied to the Ni- Foam. At last, it was dried at 60 °C for 12 hours. Then cyclic voltammetry and chronopotentiometry measurements were conducted in a potential range 0 to 0.8 (V). The measurements were performed using Electrochemical Analyzer. The specific capacitance (Csp) was calculated from the discharge curve using equation (2).

4.4.4 Iodine Number

a) Preparation of Sodium thiosulphate solution

The 0.1N solution of sodium thiosulphate was prepared by dissolving 24.818 g of sodium thiosulphate in distilled water in 1000 mL volumetric flask and diluted up to the mark with distilled water.

b) Preparation of (0.1N) $K_2Cr_2O_7$ solution

Decimolar solution of potassium dichromate was prepared by dissolving dried 7.35 g of potassium dichromate crystal in distilled water in 250 mL volumetric flask and diluted up to the mark with distilled water.

c) Preparation of iodine solution

Solution A was first prepared from 6.35 g of iodine crystal in 25 mL distilled water. Solution B was prepared from 9.85 g of potassium iodide in 25 mL distilled water. Then, iodine solution of 0.1N concentration was prepared by mixing 5 mL solution A and 5 mL solution B in a beaker with continuous stirring. And then the solution was allowed to stand for 4 hrs to ensure complete dissolution of iodine crystal. The solution was transferred in volumetric flask of 500 mL capacity and distilled water was added up to the mark. Flask was shaken well to make the solution homogeneous. The solution was rightly enclosed in dark to ensure to cut off the light radiation.

d) Preparation of starch solution

One gram of starch was taken into 10 mL of distilled water and paste was made. Then 90 mL of boiled water was poured in that solution to make it 100 mL. Later, the solution was boiled for 5 min and cooled to room temperature.

e) Standardization of sodium thiosulphate

Sodium thiosulphate was standardized by standard 0.1N $K_2Cr_2O_7$ solution. First of all, 15 mL of H_2O was taken in 250mL conical flask. Then 15 mL of 10% KI and 10 mL of 10% $NaHCO_3$ was added in it and shaken well. After that 3mL of conc. HCl was added slowly and gently shaken to mix that liquid. The 25 mL of 0.1N $K_2Cr_2O_7$ solution was added in that solution and the side of flask was washed with little water. Mixture was covered with a watch glass, shaken well and was kept in dark for about 5 minutes. The watch glass and inner wall of conical flask was rinsed with distilled water so as to trap vaporized Iodine in the solution. The solution was titrated against sodium thiosulphate solution with constant shaking until yellowish green color appeared. About 1 mL of freshly prepared starch solution was added. The blue color was obtained. On continuous addition of sodium thiosulphate solution, the color changed from blue to light green. The volume of thiosulphate consumed was noted and its concentration was calculated. After calculation, the concentration of sodium thiosulphate was determined to be 0.1N.

f) Standardization of iodine solution

Prior to determination of iodine number, the iodine solution was standardized by using standard sodium thiosulphate solution. The 25 mL of iodine solution was pipetted out and transferred into a 250 mL conical flask and was titrated with standardized sodium thiosulphate solution until the iodine solution was light yellow color. Few drops of starch indicator were added and titrated continue drop wise until colorless solution is observed. The volume of thiosulphate solution from burette was noted and the concentration of iodine was calculated. After calculation, the concentration of iodine was determined to be 0.074N.

g) Preparation of 5% Hydrochloric acid solution by weight

To prepare 5% HCl, 275 mL of distilled water was taken in a Glass Jar and 35 mL of Conc. HCl was added to it and shaked well.

h) Determination of iodine number

5mL of 5% HCl was kept in three conical flasks. To each flask, 0.1g of sample was added. The mixture was then boiled and allowed to cool at room temperature. Subsequently, 10mL of 0.074N iodine was added to each flask, and the flasks were placed on a shaker for 15 minutes. After allowing the mixture to settle, it was filtered using Whatman filter paper. The obtained filtrate was titrated with $Na_2S_2O_3$ until yellow colour appeared. A few drops of starch were then added, resulting in dark green colour, which was titrated until the colour disappeared.

4.4.5 Determination of methylene blue number

a) Determination of λ_{max} for Methylene Blue (MB)

A stock solution of methylene blue with a concentration of 500 mg/L was prepared by dissolving 0.25g of hydrated methylene blue crystals in distilled water within a 250 mL volumetric flask, subsequently diluted to the mark. From this stock solution, dilutions to 100 mg/L and 10 mg/L were made. Further dilutions were performed using a serial dilution method to achieve concentrations ranging from 1 to 9 mg/L. The absorbance of a 5 mg/L solution was measured using a UV spectrophotometer to determine the maximum absorbance (λ_{max}) corresponding to the concentration of methylene blue plotted on a graph.

b) Determination of MB number

In a conical flask, 50 mL of a 100 mg/L MB solution was carefully measured and 0.025g of as prepared AC was added. The mixture was thoroughly shaken to ensure proper dispersion. Subsequently, it was placed in a Rotatory Flask Shaker for 5hrs at 200 rpm to facilitate the adsorption process. Following this, the solution was allowed to settle for 24 hours, followed by filteration of the solution. The absorbance of MB solution was then determined using UV Spectrophotometer at its maximum wavelength (λ_{max}). Finally, the MB concentration was calculated using the formula from equation (5) and (6) page no. 9.

c) Determination of specific surface area of the WS material

To determine the surface area of walnut shell adsorbent material, Langmuir adsorption isotherm model has been used. In this study, methylene blue (MB) adsorption method was applied.

To carry out MB adsorption, first of all, λ_{max} and calibration curve was obtained. Here, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 mg/L solution of methylene blue was prepared in different volumetric flasks by diluting 500 mg/L stock MB solution. The λ_{max} was measured at wavelength ranging from 400 to 4000 nm using UV Spectrophotometer.

To obtain calibration curve, the absorbance of all solution were recorded at maximum wavelength. A graph of absorbance as a function of concentration was plotted and this calibration curve was used to determine for equilibrium concentration of methylene blue solution.

To determine the surface area of walnut shell material, the batch adsorption method was used. At first, 25 mg of as prepared walnut shell derived AC was weighed accurately and transferred to adsorption bottle containing varying concentration of Methylene blue solutions i.e. 25 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, 200mg/L, 250 mg/L.

The solutions were then allowed to shake for 5hrs in mechanical shaker at 220 rpm. It was then settled down to obtain the supernant solution and remove the adsorbent material. The absorbance of the resultant solution was noted at maximum wavelength. Then Langmuir isotherm was plotted using equilibrium concentration/ equilibrium adsorption as a function of equilibrium concentration. From the Langmuir adsorption isotherm, Qm value was calculated. Then specific surface area of as prepared walnut shell derived AC was determined using **equation (7) page no.10.**

CHAPTER V

5 RESULTS AND DISCUSSION

5.1 Scanning Electron Microscopy (SEM)

The surface morphology of chemically modified carbon sample has been studied by Field Emission Scanning Electron Microscopy (FE-SEM). The FTIR spectra is shown in **Figure 4**. The **Figure 4** revealed that phosphoric acid treated carbon was found to be layered and rough in structure. A number of pores were clearly seen at the surface which is expected to have enhanced surface area.

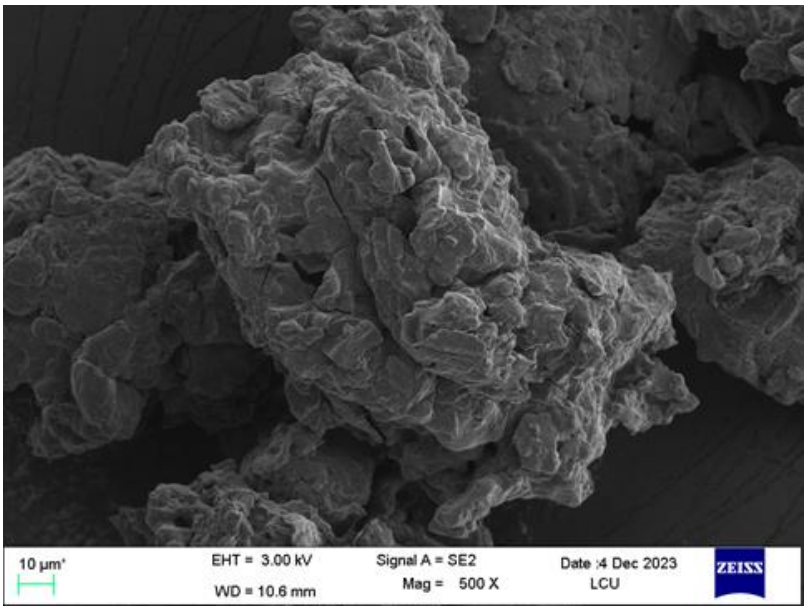

Figure 4: SEM image of WS-1

5.2 Fourier Transform Infrared Spectroscopy (FTIR)

The functional group analysis of preheated, phosphoric acid treated and activated carbon carbonized at 400 °C has been carried out. **Figure 5** shows the FTIR spectra of as prepared samples. In WS-3 the surface functional group are not very obvious while in WS-2 some bands are seen. However, in WS-1 which was chemically activated and carbonized at 400°C, more clear bands was seen. A broad band at around 3443 cm^{-1} was observed which indicates the presence of phenolic group/alcoholic group of cellulose. The band at 1743 cm^{-1} indicates the presence of –C=O stretching vibration of ketones, aldehydes or carboxylic group. Presence of a band at 1607 cm^{-1} indicates the stretching vibration of carbonyl group. The broad peak appeared in the range of

3200-3500 cm^{-1} is assigned to stretching vibration of O-H bond in alcoholic or phenolic groups. Stretching of C-O bond in ether, phenol or lactone groups is also observed in the range 1000-1200 cm^{-1}.

The several peak observed in the spectra provide information about the presence of various surface functional groups such as –OH, >C=O, COOH and lactones in WS-1 sample. (Shin et al., 1997)

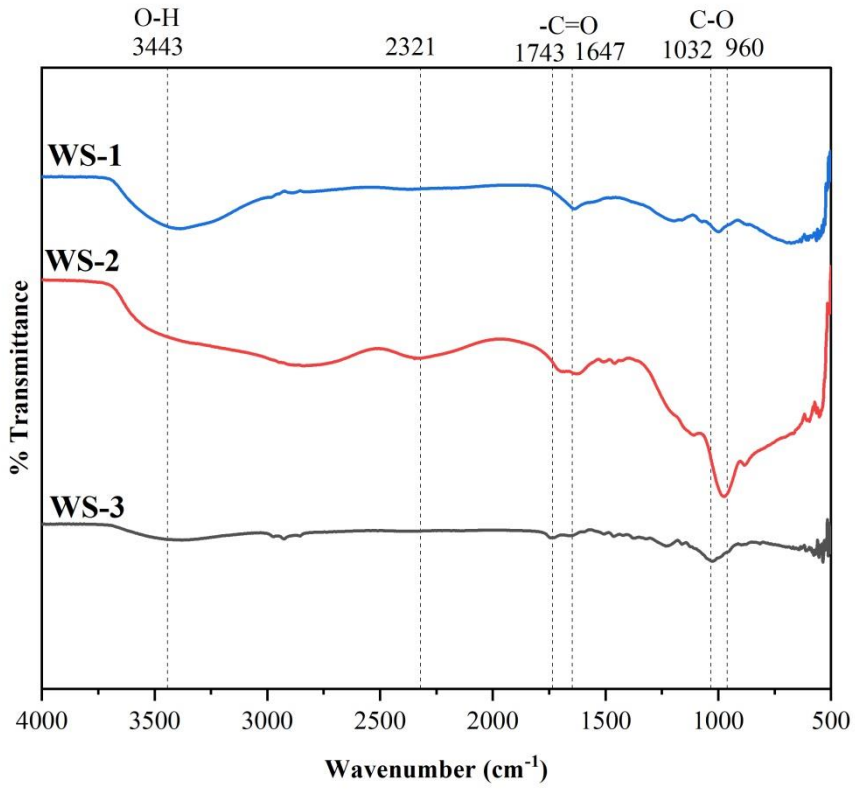

Figure 5: FTIR spectra of as samples (a) WS-1 is activated sample, (b) WS-2 is acid treated sample and (c) WS-3 is raw sample.

5.3 Iodine number

The iodine number gives the information about the micropores present in activated carbon. In this research work, iodine number of activated carbon was studied. But before carrying this experiment the sodium thiosulphate and iodine solution were standardized and prepared as of required concentration. To carry out this experiment, 5 mL of 5% HCl and 0.1 g of activated carbon was taken in conical flask and it was then boiled and cooled. 10 mL of 0.1N iodine solution was added. The solution was shaken for 1hr at 200 rpm in shaker. Solution was then allowed to settle and was filtered using whatmann filter paper. The filtrate was titrated against 0.1N sodium

thiosulphate solution. The iodine number was calculated using **equation (8).** The iodine number obtained for the samples are tabulated in **Table 2.** Results revealed that I_N value was highest in commercial sample indicating sufficient microporosity. Similarly, in as prepared AC sample (WS-1) 787.4 I_N value was obtained indicating plenty of microporosity than in WS-2 and WS-3.

Table 2: Iodine number of all four samples

S.N	Sample	Sample name	Iodine number (mg/g)
1.	Raw sample	WS-3	509.6
2.	Acid Treated	WS-2	609.6
3.	Activated Carbon	WS-1	787.40
4.	Commercial Sample	CS	999.49

5.4 MB number (MB_N)

The absorbance of methylene blue as a function of wavelength is shown in **Figure 6**. The maximum absorbance was obtained at 665nm which is used as maximum wavelength λ_{max} for the entire work.

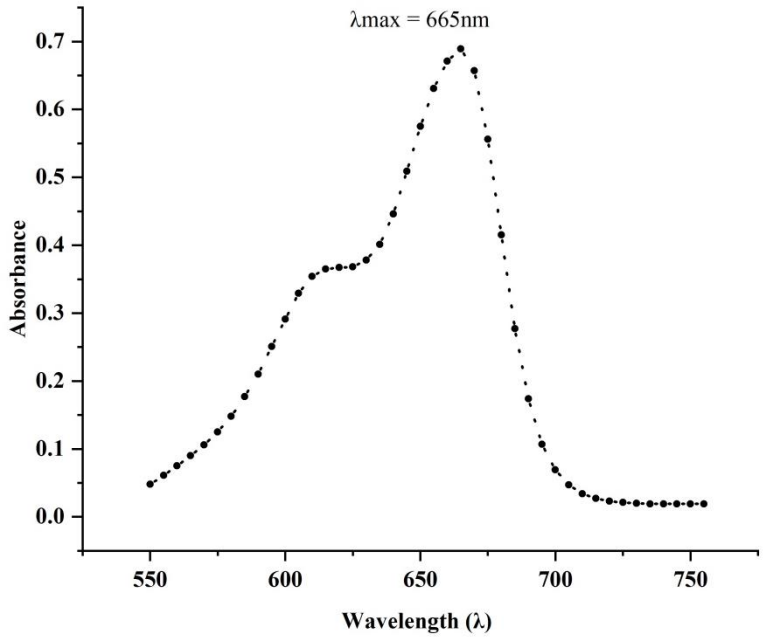

Figure 6: A plot of absorbance as a function of wavelength of methylene blue solution

The calibration curve of methylene blue solution is shown in **Figure 7.** It shows the relation between absorbance and concentration.

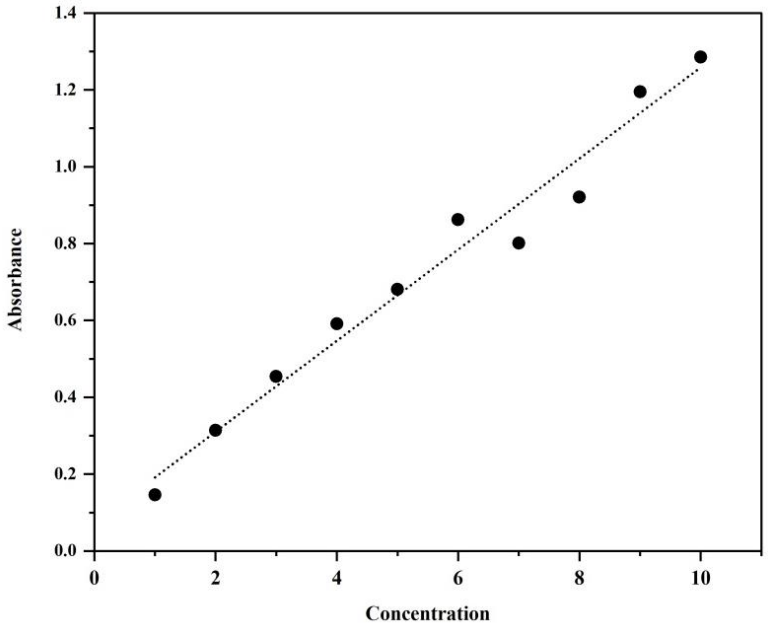

Figure 7: Calibration Curve of Methylene Blue Solution

The of MB_N WS-1 sample was found to be 181.66 mg/g which indicates the presence of mesopores on the activated carbon surface. (Bestani et al., 2008).

5.5 Surface Area

To determine the specific surface area, the Langmuir curve is drawn which is shown in **Figure 8.**

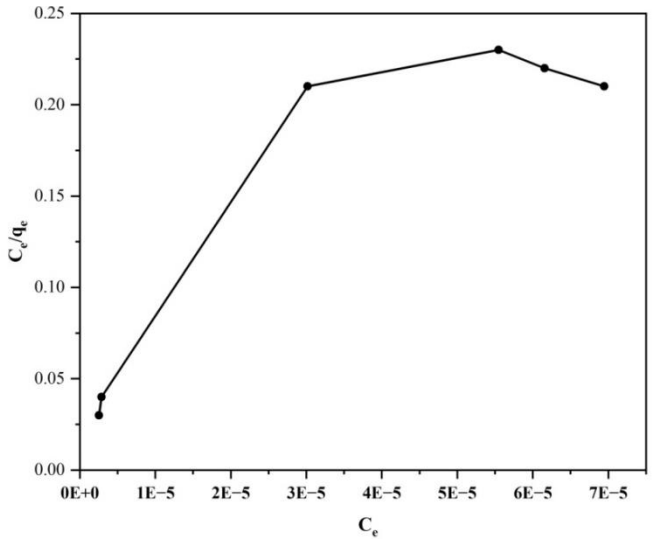

Figure 8: Curve showing Ce/qe versus Ce

The corresponding Langmuir parameters were obtained and surface area was calculated by using formula (**eq 7).** The surface area of WS-1 sample was found to be 742.71 (m^2/g).

5.6 Elecrochemical Characterization of as prepared Walnut Shell derived AC sample

a) Cyclic Voltammetry

The CV analysis was done by obtaining cyclic voltamograms which are presented in **Figure 9. Figure 9** demonstrates the material's behavior at various scan rates (5, 10, 20, 50, 80 and 100 mV/s).

From previous characterization, it has been shown that Sample WS-1 exhibited a notable surface area, pore volume, and both meso and microporous structures. These properties facilitate the diffusion of electrolyte ions, resulting in higher current responses in the cyclic voltammogram (CV) curves. Such electrochemical properties suggest the material's capactive behavior and also indicates an increase in current response with escalating scan rates, ranging from 5 to 100 mV/s. The predominant contribution to capacitance values stems from the pore structure, where solvated ions interact along the pore walls.

Moreover, the nearly rectangular shape of the curves signifies behavior similar to an electrical double-layer capacitor (EDLC), suggesting near ideal EDLC behavior. However, deviations from the ideal rectangular shape may result from impediments such as migration forces and polarized resistance, hindering electrolyte ion diffusion. Nevertheless, the mirror symmetrical cyclic voltammogram even at high scan rates, demonstrates the reversibility of the sample. The absence of pseudocapacitance in the rectangular CV curve indicates the material's capacitive behavior, where energy storage occurs purely electrostatically. Here, the lowest current response occurred at a scan rate 5mV/s, while the highest was observed at 100mV/s.

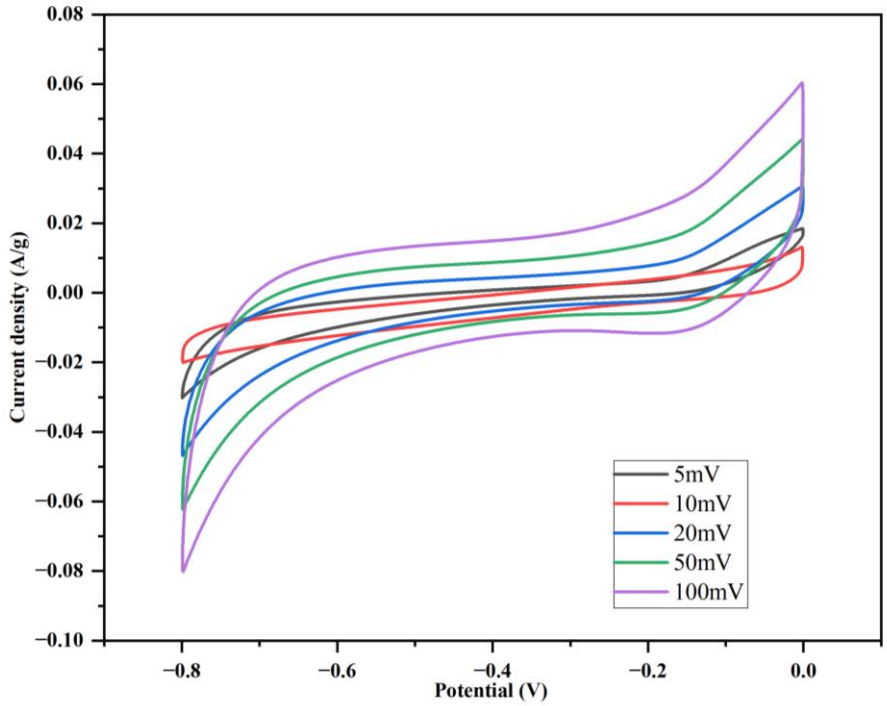

Figure 9: CV at various scan rates

Though the curves are almost rectangular in shape showing electrical double layer behavior (EDLC), the electrolyte ion diffusion may be prevented by the migration force as well as polarized resistance. This was the reason which made CV curve slightly different from ideal rectangular shape. The rectangular CV curve without pseudocapacitance reveals that the samples show capacitive behavior in which energy storage phenomenon is purely electrostatic. Table 3 shows the current response at 5mV to 100mV. Results revealed that on increasing the scan rate, the current response found to be increased from 0.01 to 0.06A.

Figure 10 shows the CV curves at scan rate and lower scan rate**.** In this Figure 10 one can see the difference in electrical behavior in 5mV and 100mV scan rate. The EDLC behavior was found to be increased after increase in scan rate whereas; it is decreased in lower scan rates. The highest current response of 0.06 A was obtained when 100 mV potential was applied.

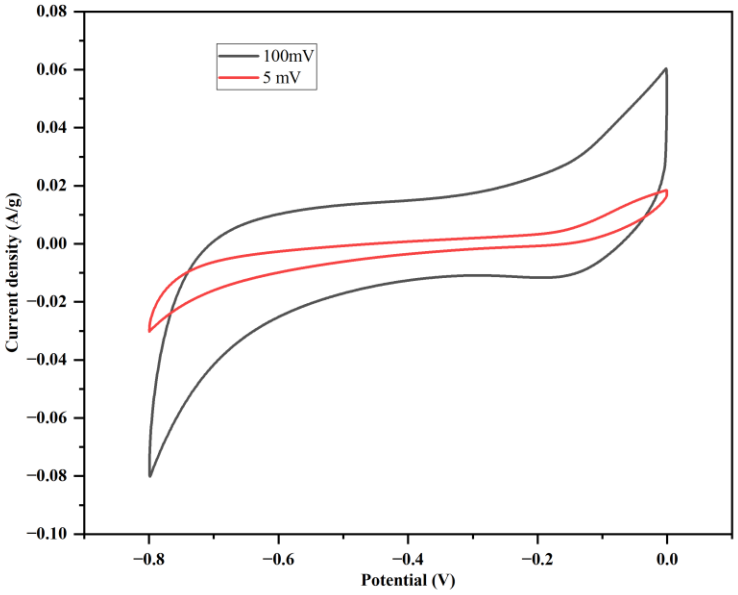

Figure 10: CV of electrode prepared from WS-1 at scan rates 5mV and 100mV

Current response was found to be lower at lower scan rates whereas higher in higher scan rates as shown in table 3.

Table 3 : Current response at different Scan rates

Scan rate (mV)	Current response (A)
5	0.018
10	0.012
20	0.03
50	0.04
100	0.06

b) Chronopotentiometry

Charge-discharge measurements were carried out by the method called as chronopotentiometry. It was done for evaluation of the electrochemical properties of walnut shell derived activated carbon (WS-1). The experiment was tested in the potential range of 0 to -1 V against Hg/HgO reference electrode at different current density ranging from 2, to 30 mA. On the basis of total mass of electrode, the charge

discharge current density was calculated. The discharge time was slower in lower current density i.e. 0.5 A/g.

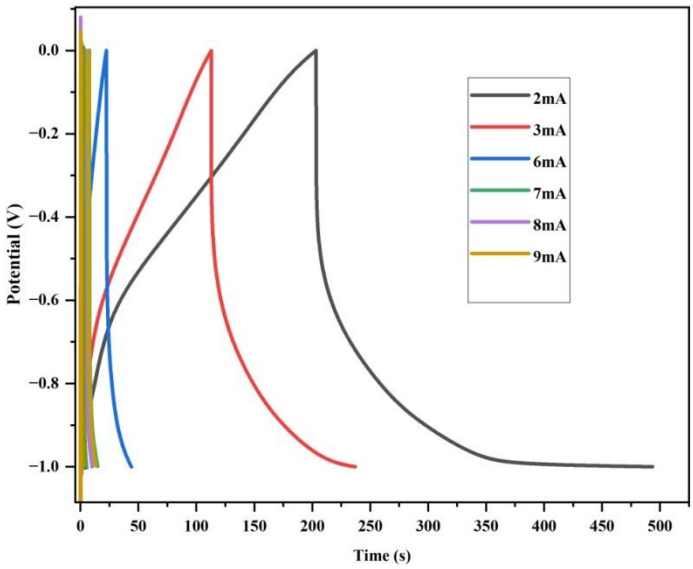

Figure 11: GCD at different current density

As can be seen in **Figure 11**, the charge discharge rate is highest at the current density value 2 mA and current density was found to be 0.5 A/g. Curves are almost symmetrical which indicates the reversibility of the electrode as well as double layer capacitive behavior.

The specific capacitance, energy density and power density was calculated by using **equation (2), (3)** and **(4)** respectively. Specific capacitance (C_{sp}) at current 2 mA was found to be 145.25 F/g. The energy density was found to be 72.63 Wh/Kg (**Table 5**) and the power density was 900 W/Kg (**Table 5)**.

Table 4 : Specific Capacitance of AC at different current densities

Sample Name	Current density (A/g)	Specific Capacitance (F/g)
WS-1	0.5	145.5
	0.8	94.22
	1.5	32.22

The Csp was found to be higher in 0.5 A/g, Then further energy and power density were also calculated which is given in **Table 5**. Similarly, ESR value was also obtained by EIS analysis. Nyquist plot is shown in **Figure 12** which is described in **section 5.6 (C)**.

Table 5: Specific capacitance, Energy density, Power density and ESR value of WS-1 sample

Sample Name	**Specific Capacitance (F/g)**	**Energy density (Wh/kg)**	**Power density (W/kg)**	**ESR (Ω)**
WS-1	145.5	72.63	900	0.5

c) Electrochemical Impedance Spectroscopy (EIS)

It is the technique used for studying the resistance in super capacitor. The electrochemical processes occurring a different time could be studied by current responses over a series of frequencies which enables distinction between electronic and ionic processes. **Figure 12** reports the Nyquist impedance plot of as prepared activated carbon (WS-1) electrode in (0.1M) KOH electrolyte which is scanned from 10 kHz to 1 mHz. The points are experimental data. The semicircle curve was linked to polarization resistance, which represents the diffusion or transport of electrolyte into the porous electrode material. (Shrestha et al., 2018). There are two capacitive loops which are obvious, one at lower frequency region and other at higher frequency region. First small loop represents diffusion impedance in parallel to double layer capacitance and second larger loop represents the charge transfer resistance with double layer capacitance.

From **Figure 12**, the ESR (Equivalent Series Resistance) value was found to be very small of 0.5Ω. It shows very small resistance at current transfer. This result is in agreement with literature value . (Shrestha et al., 2018)

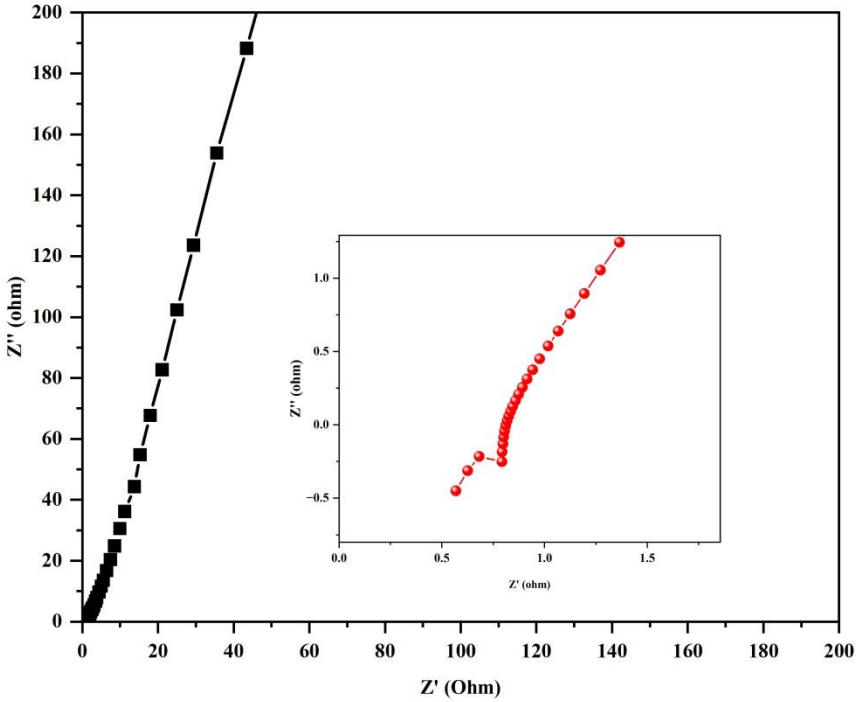

Figure 12 : Nyquist plot obtained in WS-1 sample. The enlarged plot is shown in inset picture.

CHAPTER VI

6 CONCLUSIONS

Activated carbon was successfully prepared from Walnut Shell powder through a process involving treatment with phosphoric acid followed by thermal treatment in inert atmosphere at tube furnace. The resulting activated carbon exhibited desirable surface area and porosity, which were determined using methylene blue number and iodine number methods. The iodine number, of preheated sample, acid treated sample, activated carbon and commercial carbon was found to be 509.6, 609.6, 787.40 and 999.49 mg/g respectively.

Mesoporosity of activated carbon was determined by methylene blue number which was found to be 181.66 mg/g. Similarly, the specific surface area was determined by methylene blue adsorption method which was found to be 742.71 m^2/g.

From SEM image one can see the rough and porous structure with few cracks on the surface which demonstrates the porosity development after activation.

The as-prepared AC sample WS-1 was evaluated using a variety of spectrochemical and analytical instruments, which proved the sample's porousness, and availability of functional group that allowed for the simple diffusion of electrolyte ions and conductivity.

The rectangular symmetrical CV curve confirms the EDLC behavior and, hence it gives specific capacitance of 145.3 Fg^{-1} at 0.5 Ag^{-1} current density and energy density 72.63 Wh/Kg along with a high-power density of 900 W/Kg. This can enhance ion diffusion and reduce device charge transfer resistance due to the advantageous and essential characteristics stated earlier in this paragraph. These results show that walnut shell derived activated carbon materials are widely accessible for symmetric EDLCs. The overall results/electrochemical performances showed excellent capacitive behavior of WS-1 prepared from walnut shell. It proves to be potential candidate to use as a material in electrode of supercapacitive devices.

CHAPTER VII

7 SUGGESTION FOR FURTHER WORK

From this study, it was found that walnut shell can be used as electrode material for supercapacitor. Hence, this study can be further extended in preparing low cost supercapacitor by using different type of biomass and activating in different temperatures.

Here, electrochemical measurement was done using phosphoric acid in 1:1 ratio by weight. It can also be further studied by varying the ratio and other electrolyte.

Furthermore, we can use nafion as binder and glassy carbon can be used as electrode.

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