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Preparation and Characterization of Activated Carbon from Harro (*Terminalia chebula*) Seed Stone by Chemical Activation with Phosphoric Acid for Energy Storage Devices.

by

Kirti Bir Rajguru

A THESIS
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The undersigned certify that they have read, and recommended to the Institute of Engineering for acceptance, a thesis entitled **" Preparation and Characterization of Activated Carbon from Harro (*Terminalia chebula*) Seed Stone by Chemical Activation with Phosphoric Acid for Energy Storage Devices"** submitted by Kirti Bir Rajguru, 076MSMSE008 as per the partial fulfillment of the requirements for the degree of Master of Science in Material Science and Engineering.

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Abstract

In order to meet the growing energy demand, effective energy storage devices are essential. Harro is a novel and bio-based precursor for the preparation of activated carbon (AC). In energy storage technologies, activated carbon is applied as an electrode material. By utilizing phosphoric acid as the activating agent, study examined at how the carbonization temperature affected the pore structure and surface chemistry of activated carbon from Harro seed stone. The AC was prepared at various temperatures such as 400^0C, 500^0C, 600^0C and 700^0C i.e.HS_4, HS_5, HS_6 and HS_7. By using FT-IR, XRD, SEM, Surface area, Total pore volume, Iodine number, Micropore volume, Methylene blue number and Raman Spectroscopy, study examined the physiochemical characteristics of the synthesized AC. Using cyclic voltammetry, the synthesized AC's electrochemical performance was examined. Results showed that, the activated carbon at 400^0C has the greater surface area, Iodine number and Micropore volume of 977.19 m^2/g, 960.45 mg/g and 0.69 cm^3/g respectively. And the activated carbon at 700^0C has highest value of Methylene blue number and specific capacitance of 334.72mg/g and 9.26×10^{-3} Fcm^{-1} respectively. Then, this highly porous activated carbon can be used an electrode material. Thus, the AC prepared at 700^0C is applicable for energy storage devices.

Keywords: Activated carbon; phosphoric acid; Yield; Energy storage devices

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List of Symbols

^0C	degree Celsius
Cm	Centimeter
g	gram
g/L	Gram per liter
H_2	Hydrogen
hrs.	Hours
M	Molar
m^2/g	meter square per gram
mg	milligram
mg/g	milligram per gram
mins.	minutes
mL	Mill liter
N_2	Nitrogen
Nm	Nanometer
Rpm	Revolution per minute
V	Volume of the solution
µg/day	microgram per day

List of Acronyms and Abbreviations

AC	Activated Carbon
BAC	Bead Activated Carbon
CV	Cyclic Voltammetry
FT-IR	Fourier Transform Infrared
GAC	Granular Activated Carbon
H_2SO_4	Sulphuric Acid
H_3PO_4	Phosphoric Acid
I_N	Iodine Number
I_N	Iodine Number
KOH	Potassium Hydroxide
MB_N	Methylene Blue Number
PAC	Powder Activated Carbon
RS	Raman Spectroscopy
SEM	Scanning Electron Microscope
XRD	X-ray Diffraction
$ZnCl_2$	Zinc Chloride

CHAPTER ONE: INTRODUCTION

1.1 Background

The incision of global energy demand and the exhaustion of non-renewable energy sources like fossil fuels necessitated the use of high-capacity, reliable energy storage systems. The current development in electric vehicles and high-tech electronics products places a pressing requirement on the development of reliable, large-capacity energy storage systems (Zhang et al., 2016). Because they are more affordable, environmentally friendly, and stain-resistant, electrochemical capacitors, batteries, and traditional capacitors are designed for energy storage in this regard. Batteries and super capacitors, the most common storage technologies, have both benefits and drawbacks. Batteries frequently have low power densities and high energy densities, making them better suited for large-scale energy storage. Super capacitors have a long life cycle, a high power density, and quick charge and discharge rates (Vijayakumar et al., 2018).

The materials used to create the electrodes have an impact on how well batteries and super capacitors work electrochemically. Electrodes can be made from a variety of materials, including transition metal oxides, conductive polymers, and carbon. Energy storage systems frequently use activated carbons as electrode materials because of their many fundamental properties, such as high surface area, chemical stability, high porosity, and high electronic conductivity (Ahmed et al., 2018).

Due to their advantageous qualities, such as their affordable renewable nature, eco-friendliness, and widespread availability, several bio-based materials have also received a lot of attention recently for the preparation of AC. Different agriculturally based materials, including coconut shell, rice straw, rice husk, potato peel, and other fruit seed stones, Marula seed stones, have been utilized to manufacture AC. The Harro plant is widespread around the world and is also found in Nepal. Although its seed stone was discarded, it might have been used to make activated carbon, which is a material for the electrodes of energy storage devices.

1.2 Energy storage Devices

It is projected that technologies for chemical energy storage and capacitive energy storage would play a significant role in the shift to an electrical economy. Research on the conduction of electrochemical capacitors by hybrid AC materials is summarized in

this account. Overall, using the right electrolyte and the appropriate AC electrode materials can successfully increase the amount of energy that is stored in the device as well as its power. However, neither the AC electrode materials nor the electrolyte are perfect for every material or every performance objective. Large energy density can be achieved by using AC with high surface areas and porosities that are matched to the electrolyte ion size and range from sub-nanometer to a few nanometers. As a result of the quick ion sorption and desorption on their outer surface, it can deliver high power (Boujibar et al., 2019 and Zhang et al., 2016).

1.2.1 Super Capacitors

Supercapacitos can be recognized as a major energy storage devices. It is also known as electrochemical capacitors. Supercapacitors include pseudocapcitors and electrical double layer capacitors. Supercapacitors (Scs), a special version of energy storage device, bridge the gap between conventional capacitors and batteries. Supercapacitors have a greater capacitance than conventional capacitors, allowing them to store more energy. Numerous energy storage systems in the electrical system are crucial for both functioning as a reservoir for needed power during large production peals and storing excess energy (Yaglikci et al., 2020).

Two parallel electrodes are separated from one another in super capacitors by a non-conductive material coated including an electrolyte. By drawing the electrolyte's ions to an electrode with the opposite charge when potential is applied, each electron forms an electrostatic double layer. An analogous series resistance can be added to the circuit to precisely account for all of the device's resistance characteristics (Xie et al., 2019). The capacitance of a normal capacitor can be calculated by using following formula:

$$C = \frac{\in o \in A}{d} \qquad \text{Equation 1.1}$$

Where, ∈o is the permittivity of vaccum, ∈ is the permittivity of the electrolyte, 'A' is the area of the electrode and d is the thickness of the EDL.

The capacitance of the supercapacitor can be calculated by using following formula:

$$\frac{1}{C_{dl}} = \frac{1}{C_{diff}} + \frac{1}{C_H} \qquad \text{Equation 1.2}$$

Where,

C_{dl} = EDL capacitance

C_{diff} = capacitance of diffusion region

C_H = capacitance of double-layer Stern type of compact

In EDLCs**,** charges store electro-optically through ion adsorption at the electrode-electrolyte interface.

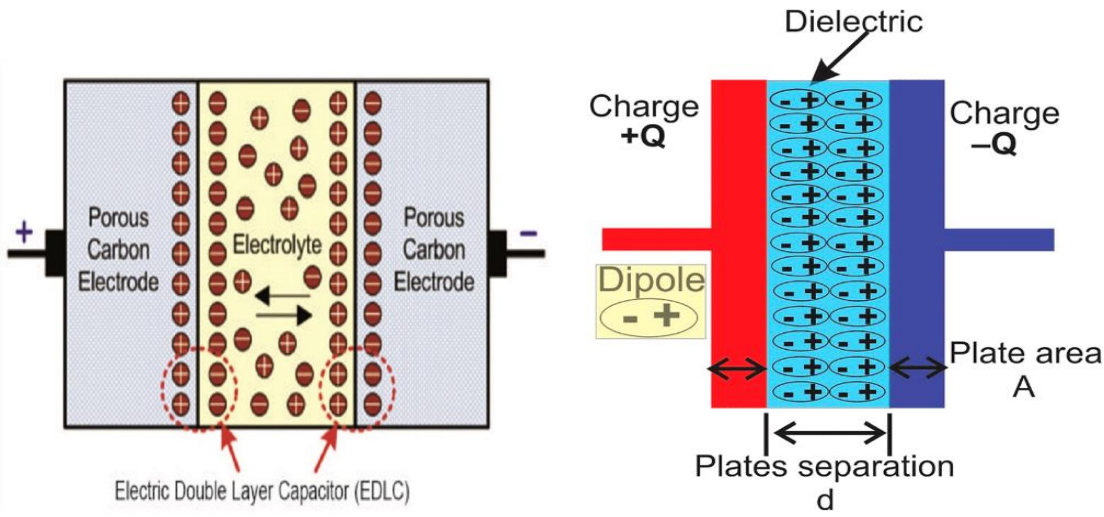

Figure1.1: (a) Supercapacitor (b) Electrostatic Capacitor

(Source: Marcelo Gustavo Molina) (Source: Faizan Ali)

Two electrode materials made of carbon, enough electrolytes, and a separator compensate an EDLC. The electrochemical double-layer storage theory allows EDLCs to retain charges without transferring them either electrostatically or by a non-Faradaic mechanism. Pseudo capacitors use a Fradaic technique to store charge that involves the electrostatic transfer of charge loads (Cheng et al., 2020). When a voltage is applied to pseudo capacitors, the electrode materials undergo reduction and oxidation, and a Faradaic current flows through the SC cell. Pseudo capacitors with higher energy densities than EDLCs are the result of this Fradaic process. Among the electrode materials used in these capacitors are metal oxides, metal-doped carbon, and conductive polymer polymers. Comparing conductive polymer SCs to carbon-based EDLCs, conductive polymer SCs have a higher capacitance, lower ESR, and lower cost. Conversely, depending on the redox reactions in the SC, pseudo capacitors also have a lower power density and a shorter life duration (Senthilkumar et al., 2013).

Conductive polymer-based SCs offer cheaper cost, higher capacitance, and lower ESR than carbon-based EDLCs. However, pseudo capacitors also have a lower power density and a shorter lifetime depending on the redox reactions in the SC. In a single cell, the hybrid SC system combines the energy sources of an electrode that resembles a battery and an electrode that resembles a capacitor. In addition to polarizable electrodes like carbon, the SC type also employs non-polarizable electrodes like metal or conducting polymer. Both Faradic and non-Faradaic materials can store a lot of energy through the two electrodes (Liao et al., 2012)

1.3 Activated Carbon

Activated carbon (AC) is a versatile group of adsorbents, countermeasures, and colorants. A significant surface area and tunable pore size are characteristics of activated carbon. Thousands of inorganic and organic compounds are grouped together under the umbrella term "activated carbon" (Laksaci et al., 2017). The makeup of a prepared AC's chemical bond and surface groups effectively defines its chemical characteristics. Surface shape, porosity, high surface area, and electro-conducting amphoteric properties are the characteristics of activated carbon (AC). The raw materials' physical and chemical properties, as well as the activation agent, have an effect on the properties of activated carbon (Ekpete et al., 2017).

The Terminalia species known as Harro is native to countries such as India, Nepal, Sri Lanka, Malaysia, and Vietnam. It is a deciduous tree that can reach a height of 30 meters and has a 1-meter-diameter trunk. Tropical and subtropical forests are where it flourishes.

Functional groups determine the general characteristics the activated carbon such as hydrophobicity, polarization intensity, adsorption and acidity. A type of carbon called "activated carbon" has been processed to contain tiny, low-volume pores, which expands the surface area open to adsorption or chemical reactions. By carbonizing the prepared carbon materials in an inert environment and activating the carbon using chemical activators, activated carbons are created. The process of physical and chemical activation can be used to prepare activated carbon with a range of pore sizes. In terms of operational procedures and mechanism, the development of porosity differs between the two ways (Ahmed et al., 2018). When Harro (Terminalia chebula) seed stone is used to make activated carbon, it transforms undesired, low-value seed stone

into beneficial, high-value adsorbent, which has an impact on both the economy and the environment. Widespread applications for AC include energy storage devices, solvent recovery, air pollution management, and wastewater treatment. A wide range of applications for activated carbon include electrodes for super capacitors, catalysts, adsorbents and additives. Additionally, because of its large surface area, meso pore structure and micro pore volume activated carbon is one of the most commonly employed material for electrodes in supercapacitors. Because it is very porous and has a greater surface area, activated carbon is an effective adsorbent and conducting substance that can be used as an electrode material (Maher et al., 2021). Therefore, activated carbon is recognized as the best electrode material for energy storage application.

1.3.1 Types of Activated Carbon

Activated carbon (AC) can be categorized into many forms based on its physical characteristics, surface features, and preparation process. However, there are general divisions of AC based on particle size, including Bead AC, Powdered AC, and Granular AC (Gottipati, 2012).

1.3.1.1 Bead Activated Carbon (BAC)

The average particle size of activated carbon beads is 0.35 mm. Made from petroleum pitch, the activated carbon is very spherical. It offers a good flowability, perfect particle size distribution, outstanding strength, and low dust content. Due to its spherical shape, it can be used in fluid bed applications like water filtration.

1.3.1.2 Granular Activated Carbon (GAC)

Raw organic materials with a high carbon content is used to create granular activated carbon. It has an average particle size of 0.6mm. Continuous procedures for both liquid and gas phase applications use granular activated carbon (GAC). Water filtering frequently use GAC. Compared to powdered activated carbon, it has advantages. Compared to PAC, it has bigger particle size, which is related to a larger surface area.

1.3.1.3 Powdered Activated Carbon (PAC)

It is pulverized carbon having particles that are less than 0.18 mm in size, with the typical particle size falling between 0.015 and 0.025 mm. It is mostly employed in liquid phase applications for severely contaminated flue gas treatment. Surface water

or ground water can be used as an electrode material to clean drinking water and decolorize food (Gottipati, 2012).

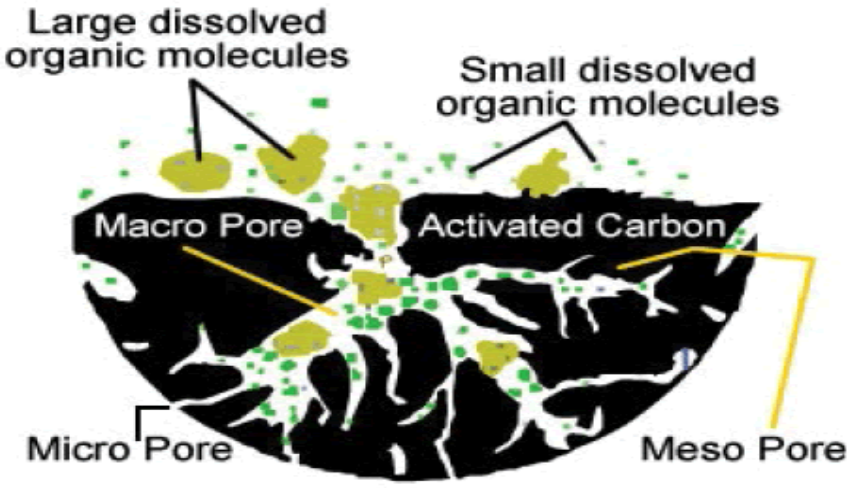

Figure 1.2: Pore Size Distribution of Activated Carbon (Slasli, 2002).

1.4 Raw Material

Harro *(Terminalia chebula*) seeed stones are economical, environmentally safe, and can be used as raw materials due to their unique chemical composition. The seed stone of Harro is hard and low ash content materials, making it a rich source of raw materials for the preparation of AC. When making activated carbon, carbonaceous materials can be utilized as the raw material. There are numerous materials utilized in the manufacturing of activated carbon, but coal-based raw materials such lignite, bituminous coal, and anthracite are the most widely used. For the creation of AC, both soft and hard raw materials have been utilized. Commercial activated carbons (AC), which are quite expensive, can be made from coal and other non-renewable sources. A medicinal plant called Harro (*Terminalia chebula*) is mostly applied in medicine. The only other component utilized to manufacture medicine is the bark. The seed was cleaned inside. Consequently, it is employed in the creation of activated carbon (AC).

1.5 Synthesis of Activated Carbon

Solid carbonaceous source materials, like Harro seed stone, can be utilized to make activated carbon. Both physical activation and chemical methods were utilized to create the majority of the carbon-rich precursors that were used to make AC. The carbonization of raw materials at high temperatures between 800 ^{0}C and 1100^{0}C in the

presence of inert gases like nitrogen characterizes the physical activation (Odetoye et al., 2019).

Chemical activation can be accomplished in one step or two. The sample is initially combined with a chemical activator that works as a dehydrating agent, such as KOH, H_3PO_4 and $ZnCl_2$ etc. (Lio et al., 2018). Better porosity activation times and activation temperatures are just two advantages that chemical activation has over physical activation. Physical activation involves two steps. It includes carbonizing basic materials, then activating them at high temperatures while using inert gas, like nitrogen (N2). The optimum temperature for activation between 400^0C-700^0C (Akpete et al., 2017).

1.6 Activated Agent

For chemical activation processes we use different types of chemical agents such as acid, base and salt. The activating agent used for synthesis of AC are phosphoric acid H_3PO_4, $ZnCl_2$, H_2O_2, NaOH, H_2SO_4, HNO_3 and KOH etc. The commonly used activating agents are KOH, H_3PO_4 and $ZnCl_2$ (Yahya et al., 2015).

Among these, I used phosphoric acid (H_3PO_4) as a chemical activating agent because phosphoric acid is non- oxidizing acid and acid catalyst, it increase the surface area. Recent research have shown that activated carbon obtained from phosphoric acid activation developed high porosity not only this but also exhibit outstanding cation exchange properties due to the presence of acid groups.

1.7 Carbonization Temperature

The box-type resistance furnace carbonized the material for 4 hours at various temperatures such as 400^0C, 500^0C, 600^0C and 700^0C. After allowing the prepared AC to cool, four samples HS_4, HS_5, HS_6, and HS_7 each representing a different carbonization temperature were created from it.

1.8 Harro Seed Stones:

According to botany, harro is a medicinal plant that belongs to the combretaceae family. Harro is known by the scientific name Terminalia chebula. 32% of this plant's weight is made up of tannin. Harro are of the pyrogallol type and include 14 hydrolysable tannins, including punicalagin, chebulinic acid, gallic acid, and chebulic acid. The diversity in the geology affects the tannin content. In addition to phenolic chemicals,

triterpenoids, flavonol glycosides, and a coumarin named chebulin that has been combined with gallic acid were also found. It also includes a number of neutrients, including minerals, vitamin C, and amino acids.

Figure1.3: Dried Harro Seed stone

In India, Nepal, Sri Lanka, Bangladesh, Malaysia, Myanmar, and other countries in Southeast Asia, harro (Terminalia chebula) is a native plant. In Taiwan, it is widely grown. More than 250 different species of the Terminalia can be found all across the world's tropical regions. Black myroblans on English and Harro in Nepali are common names for Terminalia Chebula (Chattopadhyay and Bhattacharyya, 2007).

1.9 Problem of Statement

In past decades, the various novel energy storing method in order to drew attention, because of the uprising the demand of the energy for the global population. The electrical double layer capacitors and lithium-iron batter electrochemical system for the portable electronic device and storing the energy which have been surplus available in the power grid. They are need to store the charge efficiently and quickly for converting the renewal energy to usable form. The electrical double layer capacitors are an electrochemical system for providing the energy in the fast and reliable manner because of higher capacitance and cycling number as well as fast discharging and charging system. This system relied on the specific adsorption, electrostatic adsorption and reversible electron transfer. In order to remain these features, the faultless system is required on the electrode materials. A great material for electrodes is activated carbon because of its chemical stability, strong adsorption capabilities, and high specific energy. Hence, the recent efforts are focused towards to getting the low- cost carbon-

based materials for the particles a conventional use in the electrode of the electrochemical device. Due to their unique surface area, suitable pore size distribution, variable surface chemistry properties, and relatively high mechanical strength, AC hybrids are most frequently utilized on an industrial scale as an adsorbent for the electrode materials in electrochemical devices and processes. Hence, there is need of investigation regarding the features of the AC and composite required for the electrode materials used in the energy storing devices.

1.10 Objective:

1.10.1 Main objective

- To characterize and apply the porous structure activated carbon made from Harro seed stones.

1.10.2 Specific Objectives

The specific objectives include:

- To prepare the highly porous Activated Carbon from Harro (*Terminalia chebula*) seed stones using chemical activation with phosphoric acid
- To analyze the influence of carbonization temperature on the characteristics of activated carbon.
- To characterize the Activated Carbon by using I_N, MB_N, XRD, FT-IR, Raman and SEM.
- To analyze the electrochemical performance of Activated Carbon (AC) by using CV.
- To prepare an electrode from Activated Carbon (AC).

1.11 Organization of the Dissertation

The thesis report consists of six chapters as following:

Chapter One: Introduction: This chapter includes a definition of key terms, a statement of the problems, and the report's goals.

Chapter Two: Literature Review. It reviews the literature that is pertinent to this research work.

Chapter Three: Materials and Methods: The materials and procedures utilized in the research are discussed in this chapter, and the characterization techniques are also given.

Chapter Four: Result and Discussion: This chapter includes an analysis of the findings as well as graphics illustrating the characterization, structural integrity, and effectiveness of the created activated carbons.

Chapter Five: Conclusions and Recommendations: The report's conclusion is discussed here, and future research work recommendations are also noted.

Appendix A and B contain the topic-related table and Figures.

CHAPTER TWO: LITERATURE REVIEW

The rising demand for electrical appliances has resulted in a requirement for activated carbon electrode material for energy storage systems. Activated carbon has good potential because of its large surface area, chemical surface functional group, and porosity. The greater surface area and micro porosity of AC, which is significantly influenced by the precursor material and preparation conditions, is one of its key properties. The carbonization temperature is one of the preparatory requirements. The specific capacitance of the activated carbon electrode is significantly influenced by the region of the CV curve's loop. Following is a brief summary of some of the literature on the relationship between preparation conditions and activated carbon properties:

El-Sayed et al., (2014) used phosphoric acid as an active catalyst to make corncob-based activated carbon. The precursor was impregnated with H_3PO_4 in the ratio of 1:2 and carbonized at 400^0C, 500^0C and 600^0C for constant time of 2hrs. They observed that, surface area of 700 m^2g^{-1}, 633m^2g^{-1} and 600 m^2g^{-1} were achieved at 400^0C, 500^0C and 600^0C respectively.

Zhang et al., (2016) made the activated banana peels, which were then used to make porous, high-performance supercapacitors and batteries. The BET specific surface area of the activated banana peel was 729.03 m2g^{-1}, they observed. The activated banana peel-based asymmetric supercapacitors were found to have a specific capacitance of 161 Fg^{-1} at 0.25 Ag^{-1} and 115.1 Fg^{-1} at 2 Ag^{-1}.

Joshi, (2017) prepared the activated carbon from Lapsi seed stone and betel nut. The samples were collected, rinsed in tap water and distilled water, and then dried for 12 hours at 110 degrees Celsius in an oven. Using an electric grinder, the seed stones were broken up into small pieces and ground into powder. At a second mixing step, the produced powder was combined with the activating agent (phosphoric acid) in a weight-to-weight impregnation ratio of 1:1. The mixture was then cooked until dry mass was obtained on a hot plate. After that, samples were dried for 24 hours at 110°C in an oven. The resultant carbon was dried for three hours in an electric oven at 110°C. Iodine number was 850mg/g and methylene blue number was 275mg/g, respectively.

Ekpete et al., (2017) synthesized the AC from plant and Fruit steam. The materials was impregnated with Phosphoric acid and Zinc Chloride. For one hour, the mixture was carbonized at 400^0C.

Ahmed et al., (2018) synthesized the activated carbon from rotten carrot by using $ZnCl_2$ as an activating agent super capacitor performance in different electrolytes. A mass ratio of 1:2 of $ZnCl_2$ was used to impregnate the materials and resulting mixture was heated for two hours in a tube furnace at various temperatures, including 600, 700, 800, and 900 degree Celsius. The maximal BET pore volume and surface area were discovered to be 0.9294 cm^3g^{-1} and 1154.99 m^2g^{-1}, respectively. The produced AC-based electrode has the largest specific capacitance at basic electrolyte, measuring 135.5 Fg^{-1}, they reported.

Vijayakumar et al., (2018) prepared the activated carbon fibers electrodes for super capacitors. For the creation of activated carbon, they employed waste cotton as a raw source. Cotton waste fibers were impregnated in a 1:3 weight ratio with KOH, and the resulting mixture was carbonized to increase the micropore volume and sp. Carbon fibers had outstanding gravimetric and volumetric capacitances of 112 Fg^{-1} and 74 Fcm^{-3} at Ag^{-1}, respectively, with surface areas of 0.69 cm^3g^{-1} and 1550 m^2g^{-1}.

Luo et al., (2018) prepared the activated from rice husk residues with phosphoric acid activated. They found that, the carbonization temperature (500^0C) was the optimum temperature for the preparation AC from rice husk residues with H_3PO_4 for 2hrs. Result Showed, the maximum surface area of 1365m^2g^{-1}.

Boujibar et al., (2019) prepared the activated carbon with exceptionally high surface area from natural anthracite for supercapacitor applications. They used Sodium hydro oxide (NaOH) and Potassium hydro oxide (KOH) as an activated carbon. They found that the prepared AC with BET surface area of 2934.60 m^2g^{-1} with Potassium hydro oxide (KOH) and 1199.62 m^2g^{-1} with KOH and 1199.62 m^2g^{-1} with NaOH respectively. The highest value respectively. The highest value of specific capacitance up to 192.15 Fg^{-1} and 135.19 Fg^{-1} at el 0.1 Ag^{-1} and 2 Ag^{-1} specific current respectively.

Saad et al., (2019) prepared AC from rice straw via activated with KOH. The rice straw was impregnated with KOH by soaking for 24 hours in a weight-to-KOH-solution (13M) solution. The results material was activated at temperature 650, 750 and 850^0C under N_2 gas flow (100 ml/min) for 2 hr. It was obtained that rice straw AC showed

surface area ranging from 520 to 1048 m^2g^{-1}. The surface area of AC derived from rice straw increased with increasing activated temperature from 650 to 850^0C and found highest surface area 1048 m^2g^{-1} at 850^0C.

Mkungungwa et al., (2021) synthesized the activated the activated carbon from the Marula Nutshell. This studied primary goal was to synthesize and analyze AC made from Marula nutshells. As the concentration of the reducing agent was raised, the yield of the AC produced at 200^0C and activated with H_2SO_4 decreased. However, it can be noted from this investigation that samples activated with H_3PO_4 at 500^OC generated a significant amount of carbon. The iodine content of the synthesized AC samples ranged from 915 to 1075 mg/g. The greatest iodine value was found in AC samples activated with 40% H_3PO_4 at 500^0C, which was 1075.7 mg/g.

Maher et al., (2021) Utilizing an electrolyte containing potassium bromide as a redox additive, they created an activated carbon electrode with a promising Sp. capacitance for use in capacitors. They prepared carbon electrode by using AC powder (18mg), graphite (4mg) and 2mg of PVDF as a binder. They found that the prepared electrode showed a high Specific Capacitance of 957 Fg^{-1}.

Wei et al (2021) made the activated carbon from sugarcane tips using KOH activation as an electrode material for super capacitor use**.** The mixture was carbonized at 500^0C and 600^0C for 2 hrs. under inert atmosphere should that, the prepared AC has a large surface area of 1206.85 m^2g^{-1} and they found that, the high specific capacitance of 25g Fg^{-1} at 0.5 Ag^{-1} in 6 M KOH basic electrolyte solution.

Ospino et al., (2022) prepared the activated carbon from cassava peel. Sulphuric acid (98%) and potassium hydroxide (85%) and phosphoric acid (1:3) were used to impregnate the material for two hours. To determine the electrochemical performance, they employed cyclic voltammetry and galvano-static charge-discharge in a three electrode system. They discovered that the highest specific surface was 398.46 m^2g-1 and the highest specific capacitance was 64.18 Fg-1.

Njewa et al., (2022) Synthesized and characterized the activated carbon from Agro-wastes materials (Such as rice husk and Irish Potato Peel by sodium hydroxide and (40%) Ortho phosphoric acid chemical activated, respectively. The Irish potato peel powder were impregnated with 40% Ortho-phosphoric acid in a ratio of 1:1, 1:1.7, 1:2.5 and 1:3. The mixture was carbonized at various carbonization temperatures such as

400^0C, 500^0C, 600^0C and 700^0C for 1.5 hrs. They discovered that compared to commercial activated carbon, synthesized activated carbon provided an iodine number of 420 mg/g. On the other hand, rice husks yielded more iodine value than AC made from potato peels.

Research Gap

Solving global problems requires the use of organic and local materials. There have not been any studies on the fabrication of electrode materials for supercapacitor application from Harro seed stones as a percursors. This study aims to fill this gap to explore the storage properties of activated carbon from Harro seed stones.

CHAPTER THREE: MATERIALS AND METHODS

3.1 Materials Required

The Harro (*Terminalia Chebula*) seed stones were collected from Nardevi, Kathmandu, Nepal. Both normal and distilled water were used to wash the collected Harro seed stones. The sample was dried in an oven for 24 hrs at 70^0C. An electric grinder was used to compress the dry material. The crushed particles were sieved into a 300 micrometer size fraction.

3.1.1 Instruments and Apparatus

The following tools were utilized throughout the entire research project**.**

i. Horizontal tubular furnace

The activated carbon were prepared in horizontal tubular furnace (Accumax India) by using quartz tube of length 60cm and internal diameter of 3cm as shown in Figure 3.1

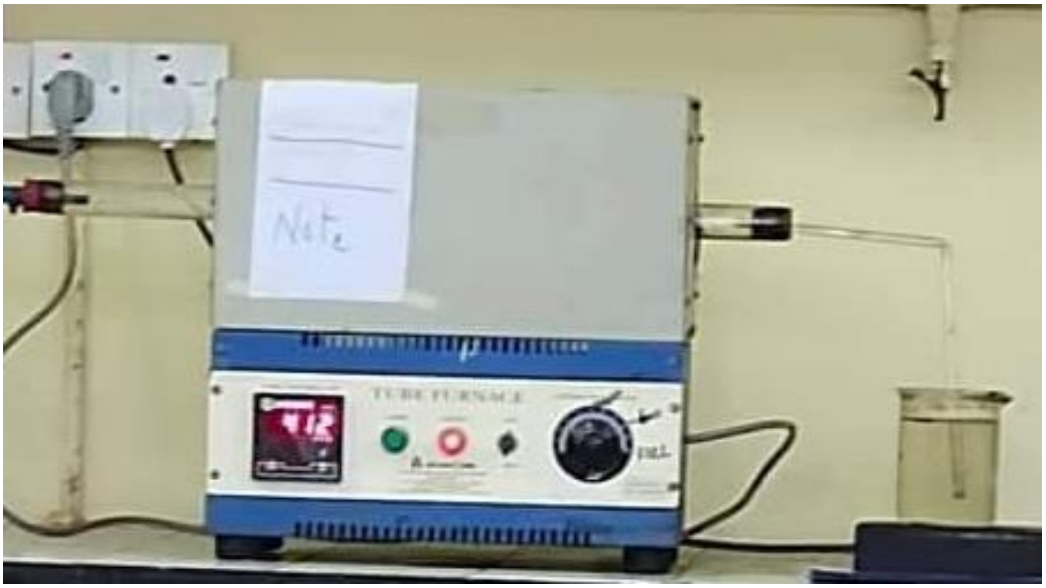

Figure 3.1: Quartz tube with horizontal tubular furnace

ii. PH meter

The PH value of different samples were maintained by using Hanna PH instrument.

iii. Hotbox Oven

The Harro seed stones and prepared AC samples were dried in the hotbox oven (Gallenkamp Registered Trade Mark Hotbox Oven).

iv. X-ray Diffractometer

The phase orientation and crystallographic analysis of prepared samples were done by XRD (NAST, Nepal).

v. FT-IR Spectroscopy

The surface functional group of prepared activated carbon was characterized by FT-IR Spectrophotometer (SHIMADZU, Department of plant Resources, Nepal).

3.1.2 Preparation of Reagents

a. 0.1N iodine solution:

   Iodine was mixed in 10% KI to make 3.175gm of 0.1N Iodine solution, which was then diluted to 250ml in distilled water.

b. 0.1M sodium Thiosulphate:

   12.39 g of sodium thiosulphate were dissolved in 500 ml of distilled water to create 0.1M Sodium Thiosulphate.

c. 5% HCl:

   Conc. HCl was dissolved in distilled water and diluted to a volume of 100 ml to create 5% HCl.

d. 1% starch solution:

   1.0 g of starch was dissolved in 100 ml of distilled water, brought to a boil, and used to create a 1% starch solution.

e. Stock solution of methylene blue:

   Methylene blue stock solution was made by combining 100 mg of the dye with 1000 ml of distilled water. By diluting the Stock solution, the necessary MB solution was created.

3.2 Preparation of Activated Carbon

Harro *(Terminalia chibula*) seed stones were collected from Naradevi, Kathmandu, Nepal. Fruits were stripped of their outer fleshy layer, and the hard, woody portion rinsed many times in distilled water before being dried for 24 hours at 700°C. An electric grinder was used to grind the dried stone. With an impregnation ratio of 1:1 by weight, a series of 15g samples were combined with 33ml of H3PO4 and swirled for two hours at 40^{o}C. The slurry has changed into a solid, sticky black color. The sample that had been impregnated was dried overnight in an oven. The sample was introduced horizontally into the center of the tubular electric furnace in a quartz tube with an

internal diameter of 3 cm and a length of 60 cm. The carbonization and activation were carried out at 400ºC – 700ºC under inert atmosphere.

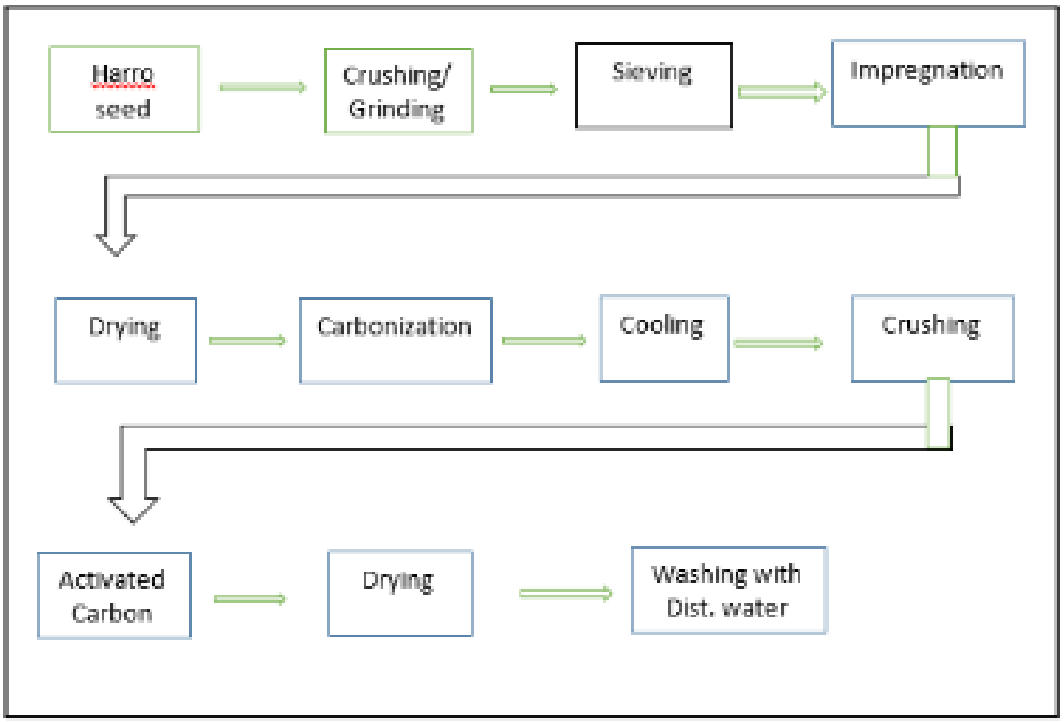

Figure 3.2: Process block diagram of Ac Production

3.2.1 Washing and Drying

The samples were cleaned with distilled and ordinary water once they had cooled to room temperature, and then rinsed with distilled deionized water using a funnel. After washing, the carbon samples were dried for 3 hours at 100 ° c in a vacuum oven. For further characterization, the dried materials were powdered and stored.

3.3 Preparation of the Activated Carbon (AC) Electrode

For the preparation AC electrodes, Activated Carbon (AC) powder, black carbon as a conduction agent and PVDF poly (Vinylene- difluoride) in the ratio of 8:1:1 were mixed with few drops of Iso-propanol to form a carbon slurry. Further, the carbon slurry of few drops were kept on the glassy carbon electrode by using micro pipette (10 µL) and then dried at 50^0C for 1hrs and 100ºC for 2 hrs.

3.4 Characterization of Activated Carbon

3.4.1 Yield Analysis of Carbon

The weight of the activated carbon that results in the weight of the Harro powder, both weights being measured on a dry basis, is known as the carbon yield.

$$\text{Yield } \% = (w_2/w_1) \times 100 \qquad \text{Equation 3.1}$$

Where w_1 represents the mass of the Harro precursor and w_2 represents the mass of the activated, washed, and dried carbon.

3.4.2 Iodine Number

Iodine number also affected how well activated carbon performed. The amount of iodine that is ingested by one gram of activated carbon is known as the iodine number. It is a measurement of the activated carbon micropore structure. The conventional procedure was used to determine the iodine number (ASTM method, 2006) (Shrestha, 2017).

5ml of 5% HCl by weight was added to 100mg of AC and left to boil for 30 minutes in order to calculate the iodine number. 10ml of 0.1N iodine solution were added once the solution had cooled. The material was violently shaken for 60 seconds before filtering. Using starch as an indicator, the filtrate solution was titrated against a 0.05M sodium Thiosulphate solution. The readings were taken down and used to compute the amount of iodine using the following formula:

$$\text{Iodine Number} = Z \times \text{Conversion Factor (CF)} \qquad \text{Equation 3.2}$$

Where,

$$CF = \frac{\text{Equivalent wt. of Iodine} \times \text{Normality of Iodine} \times 10}{\text{Wt. of Activated Carbon} \times \text{Blank Reading}}$$ (Joshi & Pokharel, 2013).

Z = blank reading – volume of Hypo solution consumed after the adsorption by Activated carbon

Blank reading = the volume of standard hypo solution needed to determine the prepared iodine solution strength.

3.4.3 Methylene Blue Number

The formation of mesoporous structure in the prepared sample is shown by the Methylene blue number. The greatest quantity of Methylene blue that may be absorbed by 1 g of the activated carbon, which is activated carbon, is measured in mg (AC). It is helpful for Figureuring out activated carbon (AC) surface area (Raposo et al., 2009).

In this procedure, 75ml of a 75mg/L methylene blue solution was in contact with 0.1g of activated carbon (AC) for 3 hours at room temperature. Intermittent shaking with an

electric shaker was then performed (Digital VDRL Rotatory –RPM-s). The formula presented below was used to compute the methylene blue number:

MB_N (mg/g) =$[(Co - Ce) * V\ ]$ M Equation 3.3

Where C_o initial concentration C_e equilibrium concentration, M is the mass the activated carbon in gram, V is the volume of the solution in liter (L) and MB_N is methylene blue number (Nunes & Guerreiro, 2011).

3.4.4 Surface Area

Using the results of the iodine number and methylene blue number, multiple regressions were used to calculate the surface area of activated carbon. The following equation can be used to calculate the surface area of activated carbon (AC) that has been prepared:

$S\ (m^2g^{-1}) = 2.28 \times 10^2 - 1.01 \times 10^{-1} MB_N + 3.00 \times 10^{-1} I_N + 1.05 \times 10^{-4} MB_N^2 + 2.00 \times 10^{-4} \times I_N^2 + 9.38 \times 10^{-4} MB_N I_N$ (Nunes and Guerreiro, 2011). Equation 3.4

3.4.5 Micropore Volume

The iodine number and methylene blue number were used in a multiple regression model to calculate the micro pore volume of activated carbon. The micropore volume can be calculated using the regression equation below:

$Vm\ (cm^3g^{-1}) = 5.60 \times 10^{-2} - 1 \times 1.00 \times 10^{-3} MB_N + 1.55 \times 10^{-4} I_N + 7.00 \times 10^{-6} MB_N^2 + 1.00 \times 10^{-7} I_N^2 - 1.18 \times 10^{-7} MB_N I_N$ (Nunes and Guerreiro, 2011) Equation 3.5

3.4.6 Total Pore Volume

Using the iodine number and methylene blue, a multiple regression model was used to calculate the total pore volume of activated carbon**.**

$V_T\ (m^3\ g^{-1}) = 1.37 \times 10^{-1} + 1.90 \times 10^{-3} MB_N + 1.00 \times 10^{-4} I_N$ (Nunes and Guerreiro, 2011). Equation 3.6

3.4.7 Fourier Transform- Infrared (FT-IR) Spectroscopy:

Utilizing FT-IR spectroscopy, the surface chemistry of the prepared activated carbon (AC) sample was examined. Sample transmission percentage was noted at a range of 500 and 4000 cm^{-1}. FT-IR spectra for all sample were recorded using SHIMADZU Spectrophotometer, Department of Plant Resources Nepal.

3.4.8 X-ray Diffraction

X-ray diffraction is a fundamental technique for determining the atomic structure and molecule spacing. A cathode ray tube creates X-rays for X-ray diffractometry, which are then filtered to produce beam of electrons, concentrated by collimation, and directed onto the sample. The basis of XRD is constructive contact of monochromatic X-rays with a crystalline sample. The detected, processed, and computed diffracted X-rays from various planes. Additionally, it is employed to determine the phase orientation and unidentified crystal structure of certain materials.

On the surface of a glass slide, activated carbon made from Harro (*Terminalia chebula*) seed stones was uniformly spread out and mounted on a Beaker D2-Phaser X-ray Diffractometer from NAST, Nepal.

3.4.9 Raman Spectroscopy

Raman spectroscopy is a type of spectroscopy that is primarily used to identify the molecular vibration mode. Additionally, it was utilized to find rotational, intermolecular, and low-frequency modes. Numerous applications in biological and material sciences are possible. Raman spectroscopy is an analytical technique that determines a sample's vibrational modes using scattered light. Depending on how much energy is transferred from the photon to the sample molecules, Raman scattering occurs. The Raman Spectrometer JASCO NRS 3000 was used to do the Raman spectroscopy.

3.4.10 Scanning Electron Microscopy

SEM is a versatile and reliable technology for analyzing materials. By scanning the surface of the sample with a laser-focused electron beam, SEM creates surface images of the sample. With a resolution of down to the micrometer and nanometer range, SEM uses an electron beam to scan the sample. The morphological properties of the prepared sample were recorded using a scanning microscope. A scanning electron microscope (SEM) is used to take pictures of processed samples. These images are typically used to determine the prepared sample's surface structure and the distribution of pores. The signals produced by the electron's interactions with the atoms in the sample provide information about the sample's surface topology, conductivity, topology, and other properties (Joshi & Pokharel, 2014).

3.5 Electrochemical Characterization

The electrochemical technique known as cyclic voltammetry measures current across an electrode as a function of potential. Basically, CV have three components such as electrode, potential and Voltammetric cell solution. Volta metric cell solution consist of two parts such as suppository electrolyte and analyte.

Analyzing the electrochemical properties of the produced carbon electrodes was done using a three electrode setup. The three electrode system consisting of a reference electrode (Ag/AgCl), counter electrode, and working electrodes was tested as an electrode for super capacitors using a cyclic voltammeter (CV) in 4M KOH electrolytes. With the help of the Corr-Test Electrochemical workstation (5.5), the capacitive activity of produced AC electrodes was detected (Awasthi et al., 2019).

The basic solution KOH is a suitable electrolyte for use as an electrolyte in energy storage applications, as shown by the symmetric I-E response curves, which exhibit good capacitive responses in the investigated potential range. At several scan speeds ranging from 3 to 20 mV/s, CV was measured using a potential window from 0 to 1V. (Liao et al., 2012). The specific capacitance of the super capacitor electrodes was calculated using an equation (Boujibar et al., 2019).

$$C_{Sp}\ (\text{F/cm}) = \frac{A}{2ka\Delta V} \qquad \text{Equation 3.7}$$

Where,

C_{SP} = Specific Capacitance

A= Integrated area under the curved

K= scan rate

m= Area of electrode

ΔV= Potential window (Vijayakumar et al., 2018).

CHAPTER FOUR: RESULTS AND DISCUSSION

The resultant carbons were subjected to a number of tests, including yield analysis, Iodine value, Surface area, Methylene blue number, Total pore volume, Micropore volume, FT-IR, XRD, SEM, Raman spectra, and CV. The effect of various carbonization temperatures and Harro seed stones powder with phosphoric acid were studied.

4.1 Materials Characterization

4.1.1 Yield analysis of carbon

Initially, the theoretical weight of Harro (*Terminalia chebula*) seed stones powder was 15g. After impregnating with 33ml of H_3PO_4 and carbonization at various temperature (400^0C, 500^0C, 600^0C & 700^0C) and drying at 100^0C the actual weight of prepared AC were 6.83g, 6.45g, 6.38g and 4.76 g respectively.

The yield of prepared activated carbon (AC) sample HS_4 at 400^0C was 45.53%, HS_5 at 500^0C was 43%, HS_6 at 600^0C was 42.53% and HS_7 at 700^0C was 31.73% respectively.

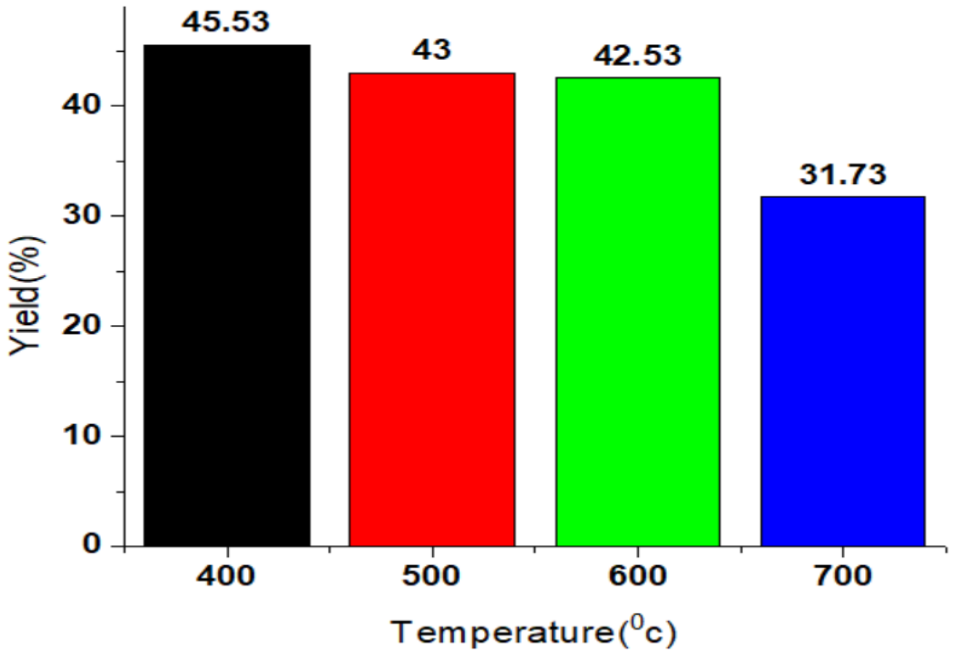

Figure 4.1: Effects of Temperature on the Yield of the AC

According to Figure 4.1: the yield of activated carbon is significantly influenced by the activated temperature. The carbon yield dropped from 45.53% at 400^0C to 31.73% at

700^0C as a result of the aromatic condensation reaction, which causes the hydro-aromatic structure of the carbonized product to evolve into gaseous products. This, in turn, increased the release of volatile substances.

4.1.2 Iodine Number

A quick and easy test method for determining the porosity structure of micro carbons is the iodine number test method. It can permeate the prepared activated carbon's deep micropores despite its small molecular size. Iodine number thus provides an approximation of the micropore count in the produced AC. Iodine number is typically employed as an indicator for the adsorbent and porosity of the activated carbon in order to calculate its surface area (AC).

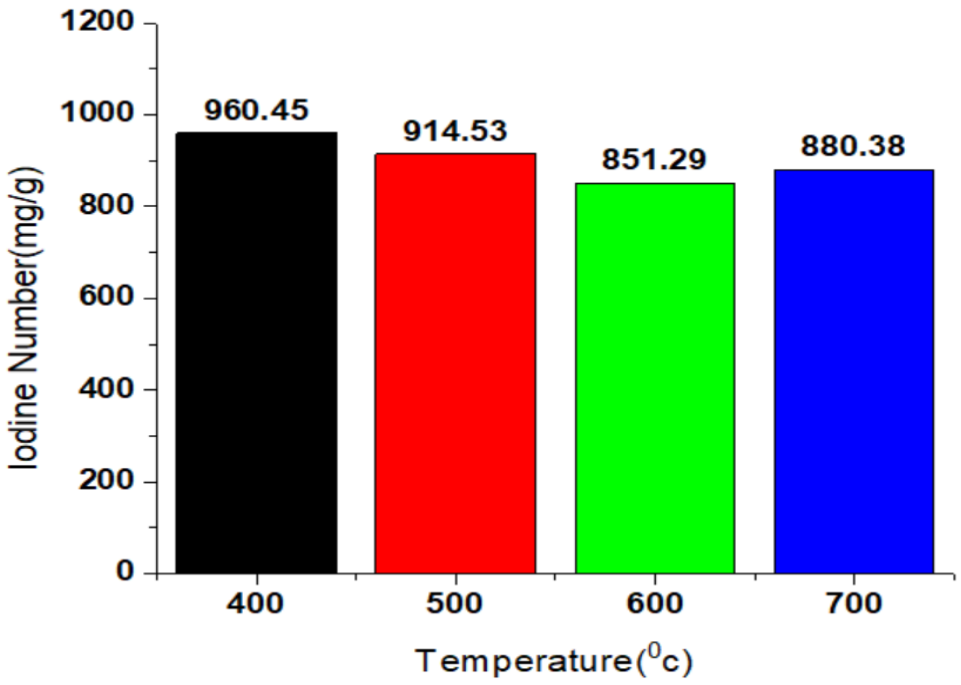

Figure 4.2: Effects of Temperature on the Iodine Number of the AC

Figure 4.2 shows how, while maintaining other variables fixed, the iodine number of activated carbon fluctuates as a function of carbonization temperature. The Figure clearly shows that the iodine number declines up to 600^{o}C before increasing. The amount of micropores can be roughly estimated using the iodine number. These results indicate that the carbonization temperature has a considerable impact on the porous system of activated carbon. The development of mesopores may be the cause of the drop in iodine number with rising carbonization temperature.

Figure 4.2: illustrates the impact of iodine number on activated carbon. Iodine number decreased with carbonization temperature, as illustrated in Figure 4.2. Iodine number maximum at 400^{o}C carbonization was 960.45 mg/g. As a result, it has been found that 400^{o}C is the ideal temperature for carbonizing Harro seed stones when phosphoric acid is used as an activator.

4.1.3 Methylene Blue Number

One quick and simple test method for determining the porous structure of mesoporous carbon is methylene blue adsorption. Activated carbon ability to absorb medium-sized particles is indicated by the mesopore distribution, or MB, in the prepared activated carbon.

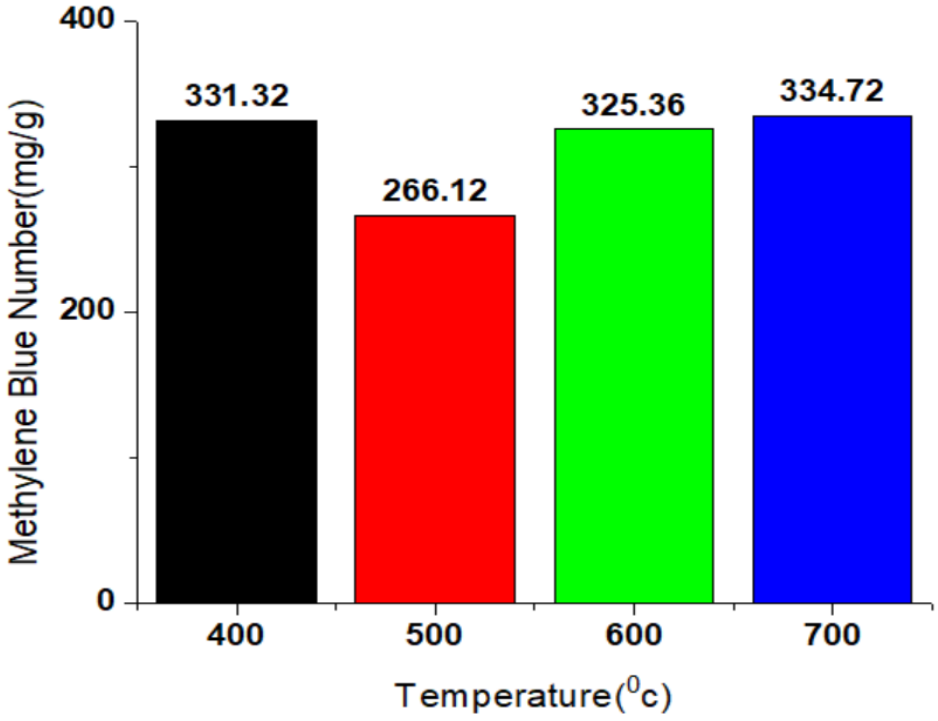

Figure 4.3: Effects of Temperature on the Methylene Blue Number of the AC

The methylene blue number of activated carbon prepared from Harro seed stones powder of different samples HS_4, HS_5, HS_6 and HS_7 at various temperatures such as 400^{0}C, 500^{0}C, 600^{0}C and 700^{0}C were 331. 32 mg/g, 266.12 mg/g, 325.36 mg/g and 334.72 mg/g respectively as shown in Figure 4.3. Characterizing the methylene blue number is mostly done to learn more about the mesopore structure on the prepared activated carbon.

4.1.4 Surface Area

The physical properties of the activated carbon prepared from Harro seed stones with at different temperatures as shown in Figure 4.4. The surface area of the prepared sample was calculated by using iodine number and methylene blue number. The value of surface area depends on the methylene blue number and iodine number. The surface area of the prepared AC were 977.19 m^2/g, 878.48 m^2/g, 866.38 m^2 /g and 901.49 m^2/g at 400^0C, 500^0C, 600^0C and 700^0C respectively. Which is comparable with commercial activated carbon.

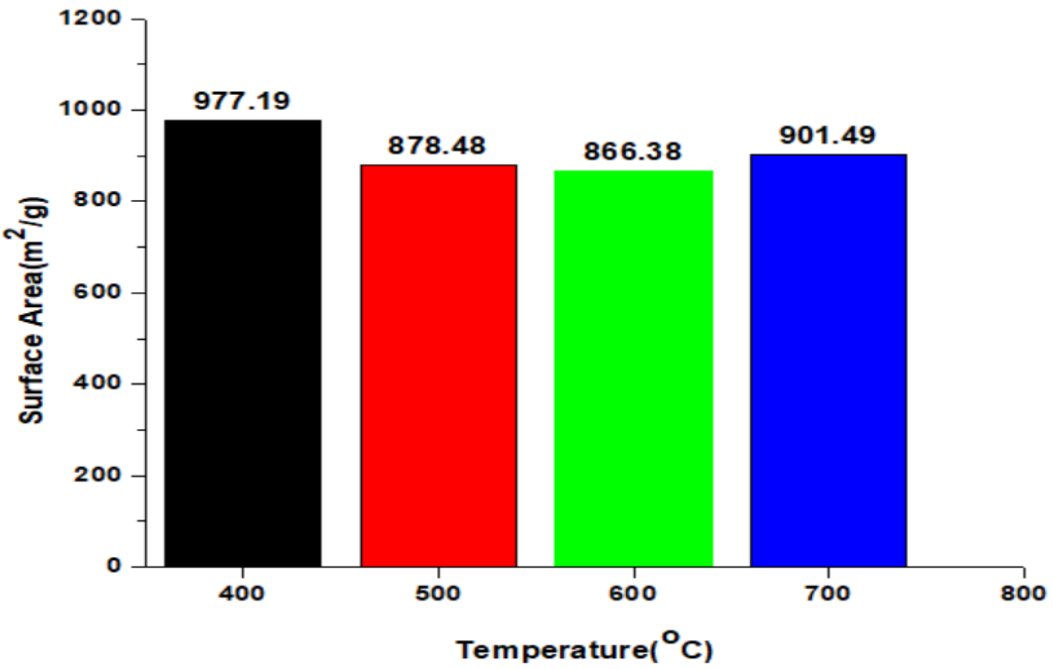

Figure 4.4: Effects of Temperature on the Surface Area of the AC.

4.1.5 Micro Pore Volume

Iodine and methylene blue numbers were used to calculate the micropore volume of the AC that had been produced. The micro pore volume of prepared AC were 0.69 cm^3/g, 0.48 cm^3/g, 0.64 cm^3/g and 0.68 cm^3/g at 400^0C, 500^0C, 600^0C and 700^0C respectively. Which is shown in Figure 4.5.

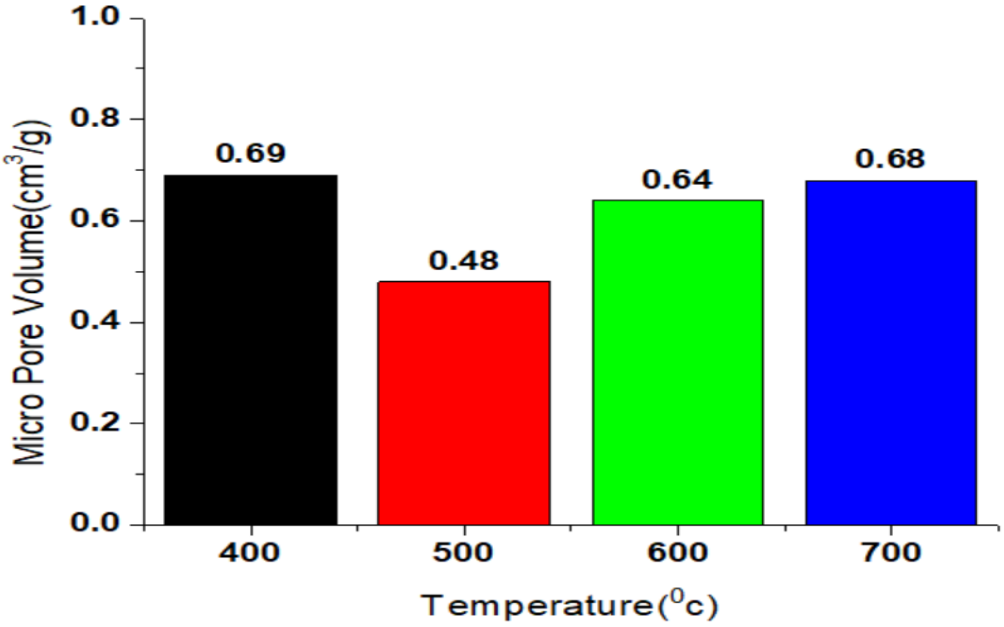

Figure 4.5: Effects of Temperature on the Micropore Volume of the AC

4.1.6 Total Pore Volume

Iodine and methylene blue numbers were used to calculate the total pore volume of the AC that had been produced. The Total pore volume of prepared AC were 0.862 cm^3/g, 0.734 cm^3/g, 0.84cm^3/g and 0.861cm^3/g at 400^0C, 500^0C, 600^0C and 700^0C respectively. Which is shown in Figure 4.6:

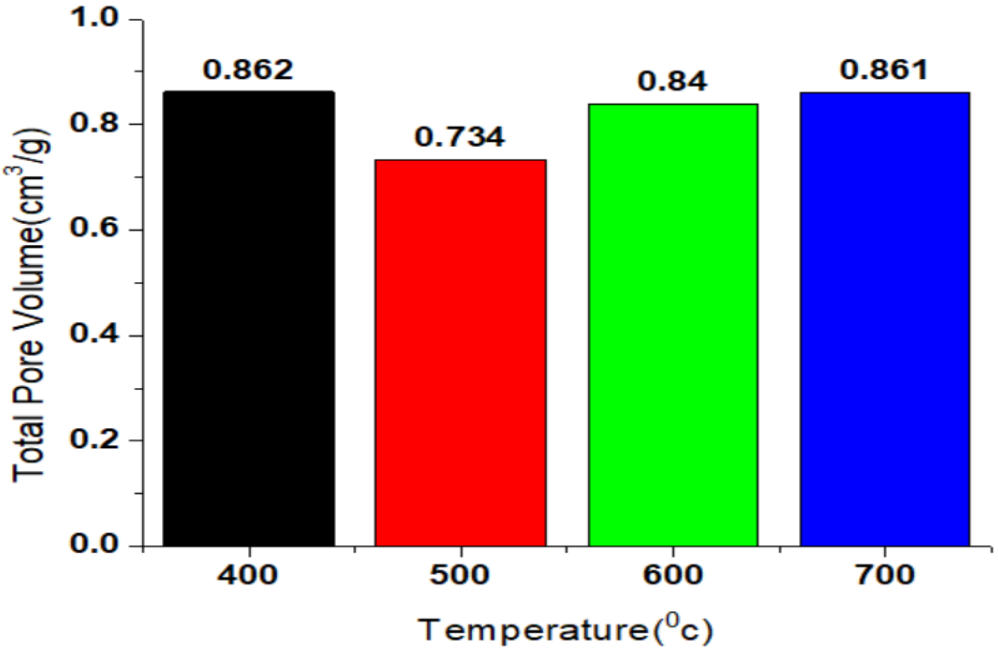

Figure 4.6: Effects of Temperature on the Total Pore Volume of the AC

4.1.7 Fourier Transform- Infrared (FT-IR) Spectroscopy

Fourier Transform-Infrared (FT-IR) Spectroscopy was used to analyze activated carbon produced from Harro seed stones in order to determine its surface functional groups. FT-IR spectra of the synthetic carbons produced by activating phosphoric acid at various carbonization temperatures are shown in Figure 4.7. The bands at 879.54 cm^{-1} in the FT-IR spectrum of the synthetic carbons HS_4 and HS_5 are caused by out of plane deformation of C-H for various substituted hydrocarbon chains. The three basic characteristic bands at 1527.62 cm^{-1}, 1550.77 cm^{-1}, and 1558.48 cm^{-1} were visible in the produced AC's FT-IR spectra.

Additionally, the C = C stretching vibrations in the aromatic ring, which is typically seen in carbon materials, caused the peak intensity of samples HS_4, HS_5, HS_6, and HS_7 to be obtained at around 1558.48 cm^{-1}, 1550.77 cm^{-1}, 1558.48 cm^{-1}, and 1527.62 cm^{-1}, respectively. The presence of the OH stretch group caused the large peak in the FT-IR spectrum sample HS_4 to be noticed at 3278.99 cm^{-1} Similar to this, the FT-IR spectrum of samples HS_6 and HS_7 shows that the OH group has been removed as a result of dehydration.

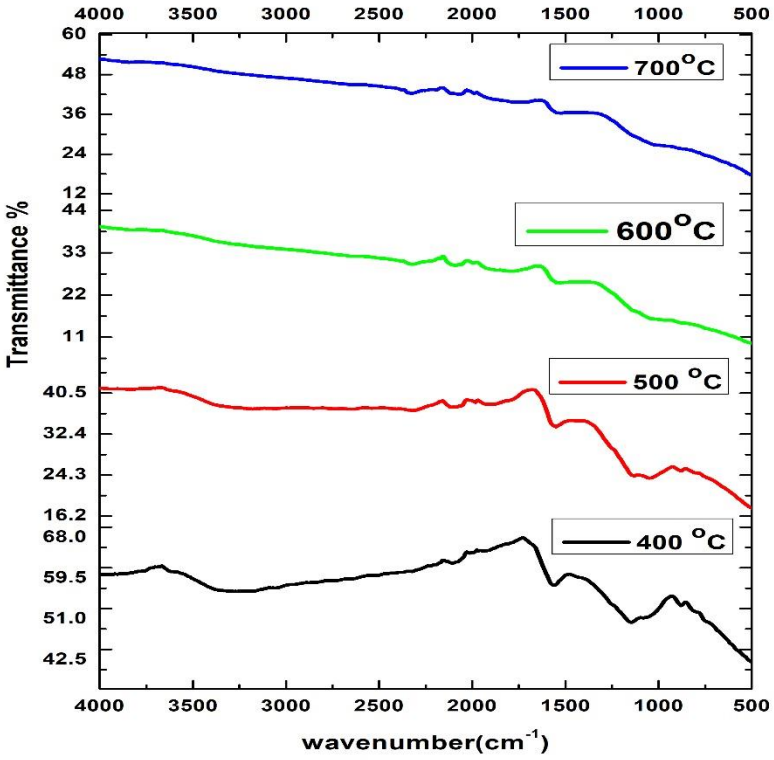

Figure 4.7: FT-IR spectrum of prepared AC at various carbonization temperatures.

4.1.8 XRD Analysis

The produced AC samples' crystal structure can be assessed using XRD. In Figure 4.8, the XRD pattern of activated carbon (AC) obtained from Harro (*Terminalia chebula*) seed stone at various carbonization temperatures was depicted.

X-ray diffraction (XRD) is mainly done for the identification diffraction pattern and phase identification. The XRD patterns of prepared AC at various temperature as shown Figure 4.8.

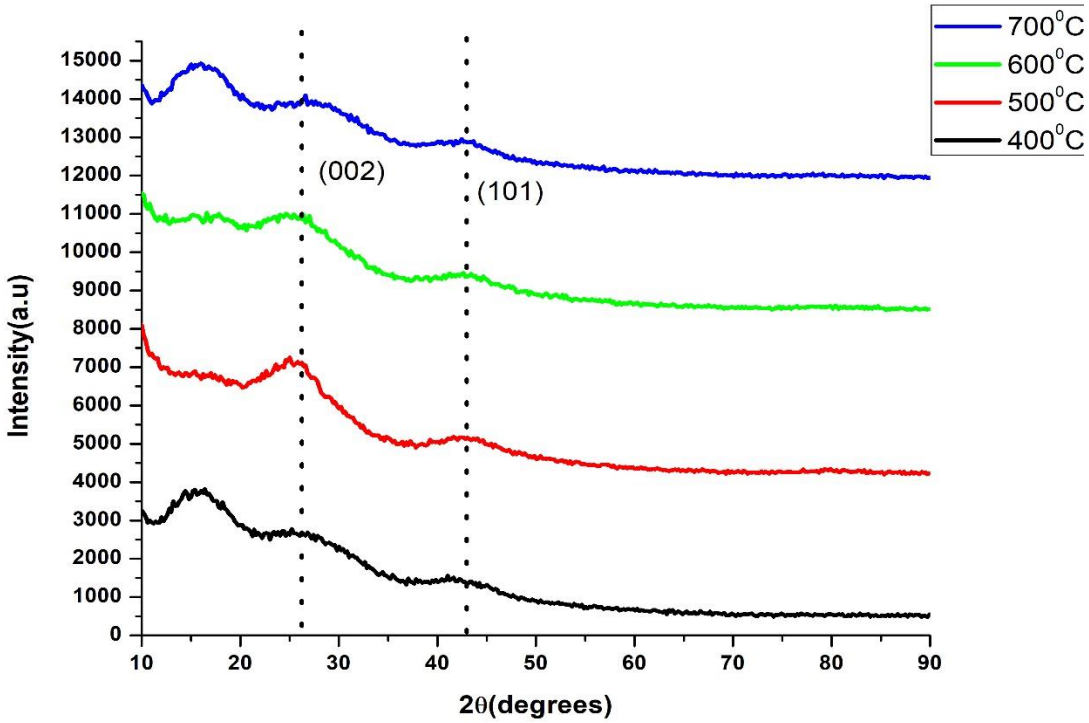

Figure 4.8: XRD patterns of prepared AC at various carbonization temperatures.

The XRD patterns of sample HS_4 and HS_6 very similar and also the XRD patterns of sample HS_5 and HS_7 are very similar. The samples HS_4 and HS_6 show broadened peaks at (18, 25) and 42.5, respectively. The samples HS5 and HS7 show Broadened peaks at (002) diffraction around 25.8 and (101) diffraction at 42.5 indicating the amorphous carbon. As the carbonization increases, the peaks of the prepared samples slightly sharpens that indicates the more ordered structure of the prepared AC.

4.1.8.1 Effect of Carbonization Temperatures on the Maximum Intensity.

As the temperature increases the max intensity decreases which shows that the sample at 400 degrees was the sample closest to the AC.

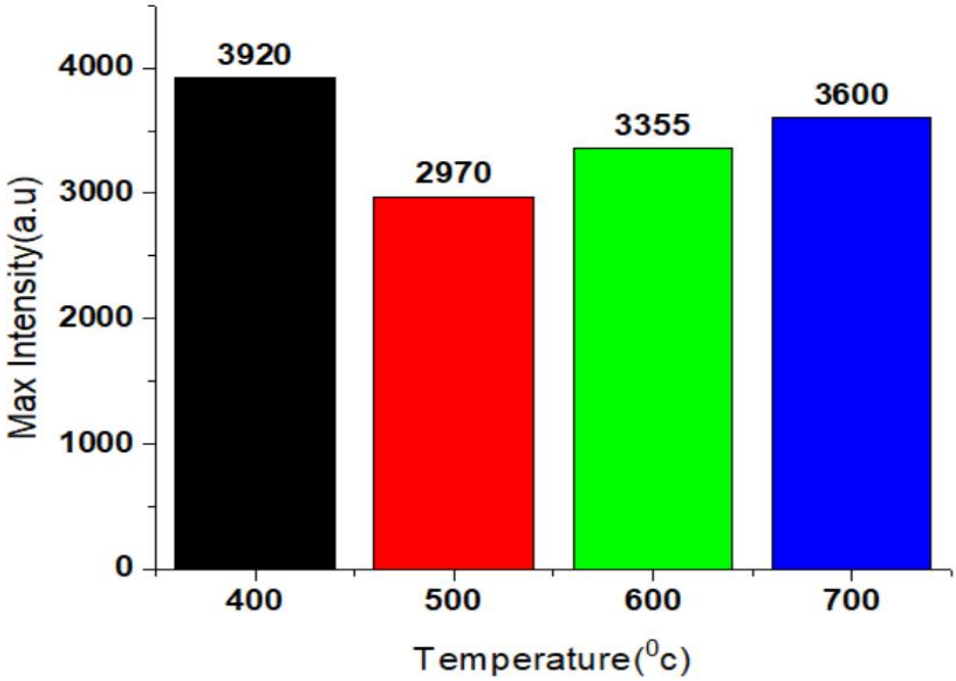

Figure 4.9: Graph of Max Intensity vs. Temperature

4.1.9 Raman Spectroscopy

The Raman spectra of various samples prepared at different temperatures were displayed in Figure 4.10: Two peaks were the most frequently seen in Raman scattering. The first peak, known as G-peak, and the second peak, known as D-peak. The lattice imperfection and low symmetry of the carbon structure are what generate the second peak, or "D-peak." With a disordered carbon structure and breathing modes of sp^2 atoms in rings, the D band's appearance in Raman scattering is connected. In a single wall carbon nanotube, the D band is absent. The symmetry and ordered arrangements in the carbon structure that resulted in the second peak (G-peak). G bands are often referred to as characteristic bands. All sp^2 atom bond stretching in both rings and chains resulted in the appearance of the G- Peak. The C-C bonds in the graphitic structure undergo in-plane tangential stretching, which gives rise to the G bands.

Semi-quantitative data on the degree of crystallization of graphitic carbon is provided by the relative ratio of intensity of the G and D bands, I (G)/I (D). A correlation exists between the imperfections and the D band's intensity. As there are more imperfections, the D band intensity rises. With more arrangement, the strength of the G band rises.

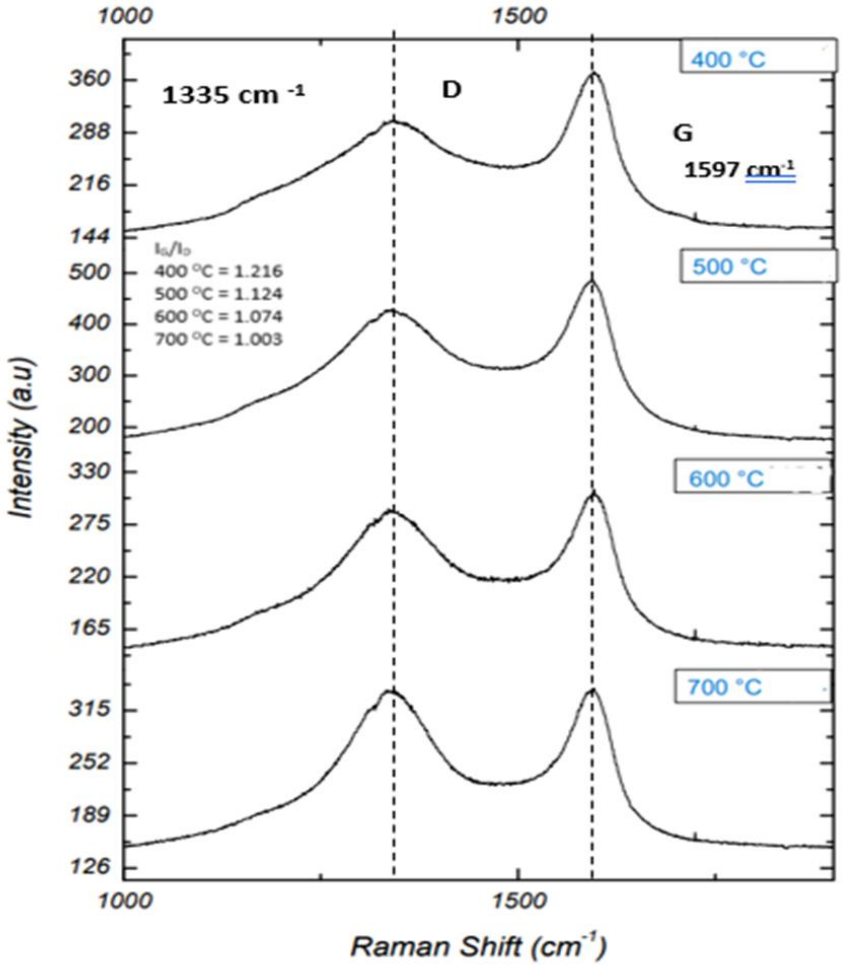

Figure 4.10: Raman spectra of the prepared AC at various temperatures

Figure 4.10 displays the two peaks in the activated carbon's Raman spectra. The D- and G-bands are located at 1335 cm^{-1} and 1597 cm^{-1}, respectively, and both of these peak positions are clearly visible in the entire sample. The intensity ratio was found to be 1.216, 1.124, 1.074, and 1.003, respectively, for a number of samples processed at different temperatures, including 400^0C, 500^0C, 600^0C, and 700^0C. All samples were found to have an intensity ratio that was close to 1. This outcome displays the semi-crystalline structure of the prepared sample.

4.1.10 SEM Analysis

Scanning electron microscopy (SEM) was utilized to examine the surface structure of the synthesized sample. Figure 4.11 depicts SEM images of activated carbon synthesized from Harro seed stones with phosphoric acid.

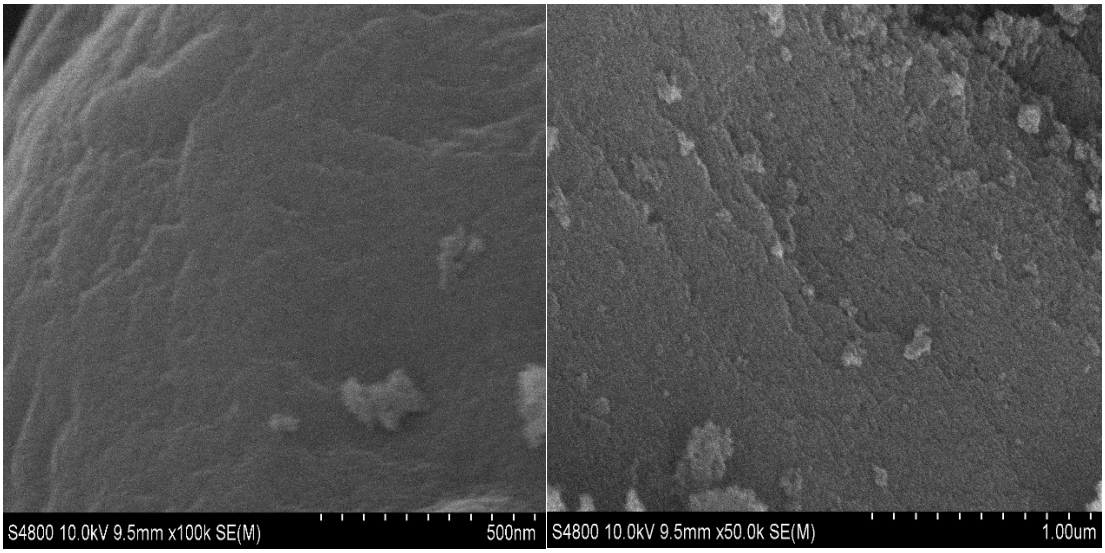

Figure 4.11:SEM images of the phosphoric acid activated AC at 700^{o}C

The SEM images of prepared AC at 700^{o}C at various scales are shown in Figure 4.11. SEM micrographs demonstrate that, the activated carbon prepared at 700^{o}C has a large number of pores on its surface. The produced activated carbon outside surface reveals a surface covered with pores. The fact that the pores have grown nicely may be related to the Harro powder's complete carbonization. As an acid catalyst, phosphoric acid is used. It enhances the breakage of bonds and the formation of crosslinks in cellulose. We can deduce from these images that the activating agent, such as phosphoric acid, evaporated during the carbonization process, leaving craters on the surface of the formed activated carbon.

4.2 Electrochemical perfomance of AC under basis electrolyte.

To evaluate the electrochemical performance of the produced samples, a three electrode setup in 4M KOH electrolyte was used. The CV curves of the produced activated carbon at various scan rates are shown in Figure 4.12 at 400 degrees Celsius. It was found that an ideal rectangular CV shape and the CV curve do not exhibit any clear peaks at 400 degrees Celsius.

The produced electrode CV curves were measured at 400 degrees Celsius at various scan rates, ranging from 3 to 20 mV/s. The CV data make it quite visible that the electrode materials achieved an ideal rectangular shape with a 5 mV/s scan rate. The electrode material demonstrates relatively smaller shape form at scan rates of 3 mV/s and 20 mV/s.

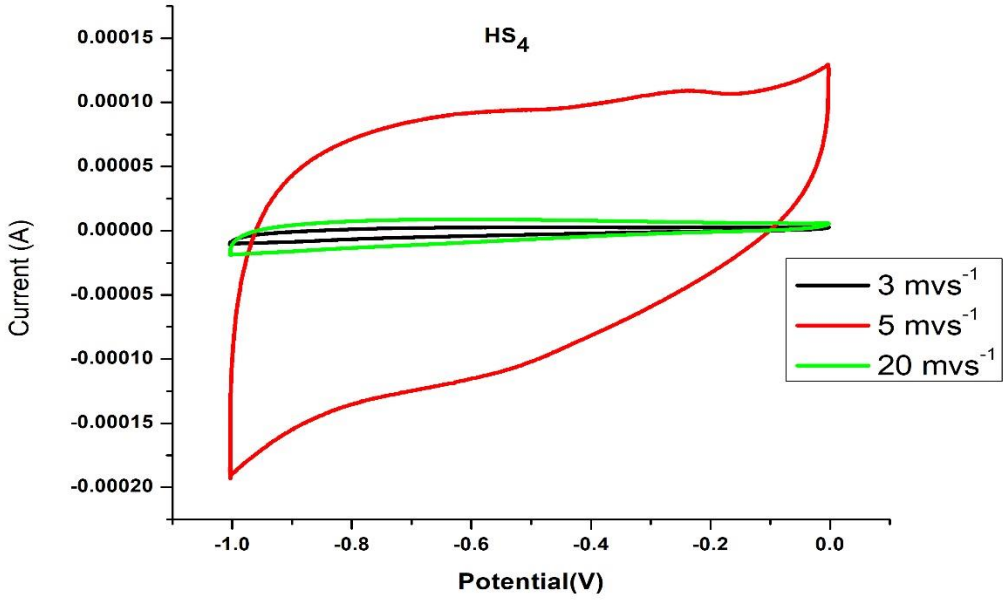

Figure 4.12: CV profile of prepared AC at 400^0C under KOH

The electrochemical behavior of the produced samples was evaluated using a three electrode system in 4M KOH electrolyte. The CV curves of the produced activated carbon at 500 degrees Celsius at various scan rates are shown in Figure 4.13. The optimum rectangular CV shape and the CV curve were determined to be devoid of sharp peaks at 500 degrees Celsius.

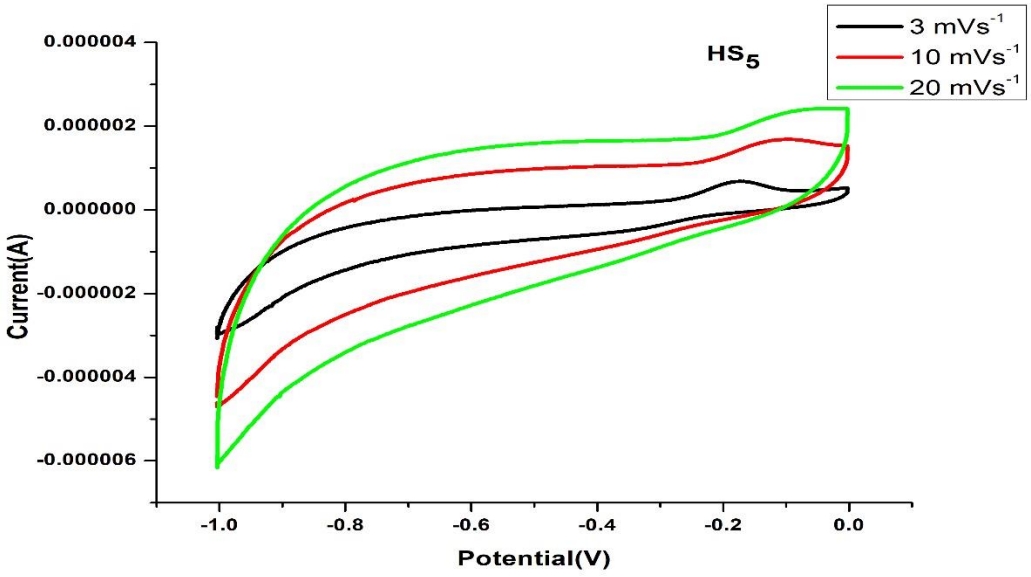

Figure 4.13: CV profile of prepared AC at 500^0C under KOH

The produced electrodes' CV curves at different scan rates, ranging from 3 mV/s to 20 mV/s, at 500 degrees Celsius. With several scan rates, such as 3 mV/s, 10 mV/s, and 20 mV/s, the electrode materials obtained an ideally rectangular form, as can be seen in the CV results.

Applying a three electrode setup in a 4M KOH electrolyte, the electrochemical performance of the produced samples was assessed. Activated carbon CV curves are shown in Figure 4.14 at various scan rates and 600 degrees Celsius. An ideal rectangular CV shape and the CV curve were found to not exhibit any strong, distinguishable peaks at 600 degrees Celsius.

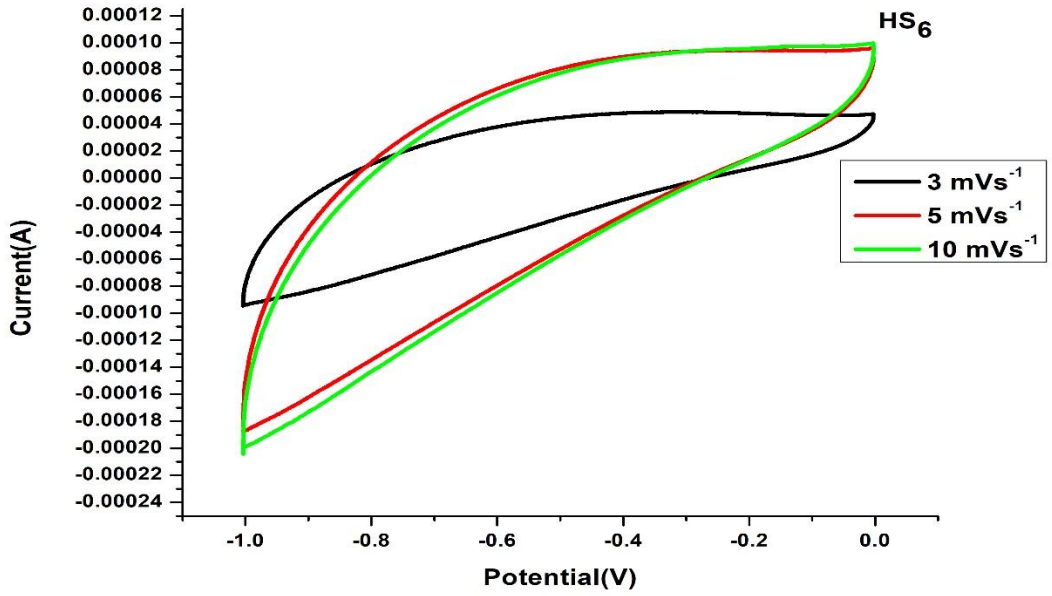

Figure 4.14: CV profile of prepared AC at 600^0C under KOH

The constructed electrodes' CV curves were measured between 3 and 10 mV/s at 600 degrees Celsius. With several scan rates, such as 3 mV/s, 5 mV/s, and 10 mV/s, the electrode materials obtained an ideal rectangular form, which can be seen in the CV results.

A three electrode system in 4M KOH electrolyte was used to assess the electrochemical performance of the generated samples. The CV curves of the produced activated carbon at 700 degrees Celsius at various scan rates are shown in Figure 4.15. At 700 degrees Celsius, it was reported that an ideal rectangular CV shape and the CV curve do not reveal any sharp, distinguishable peaks.

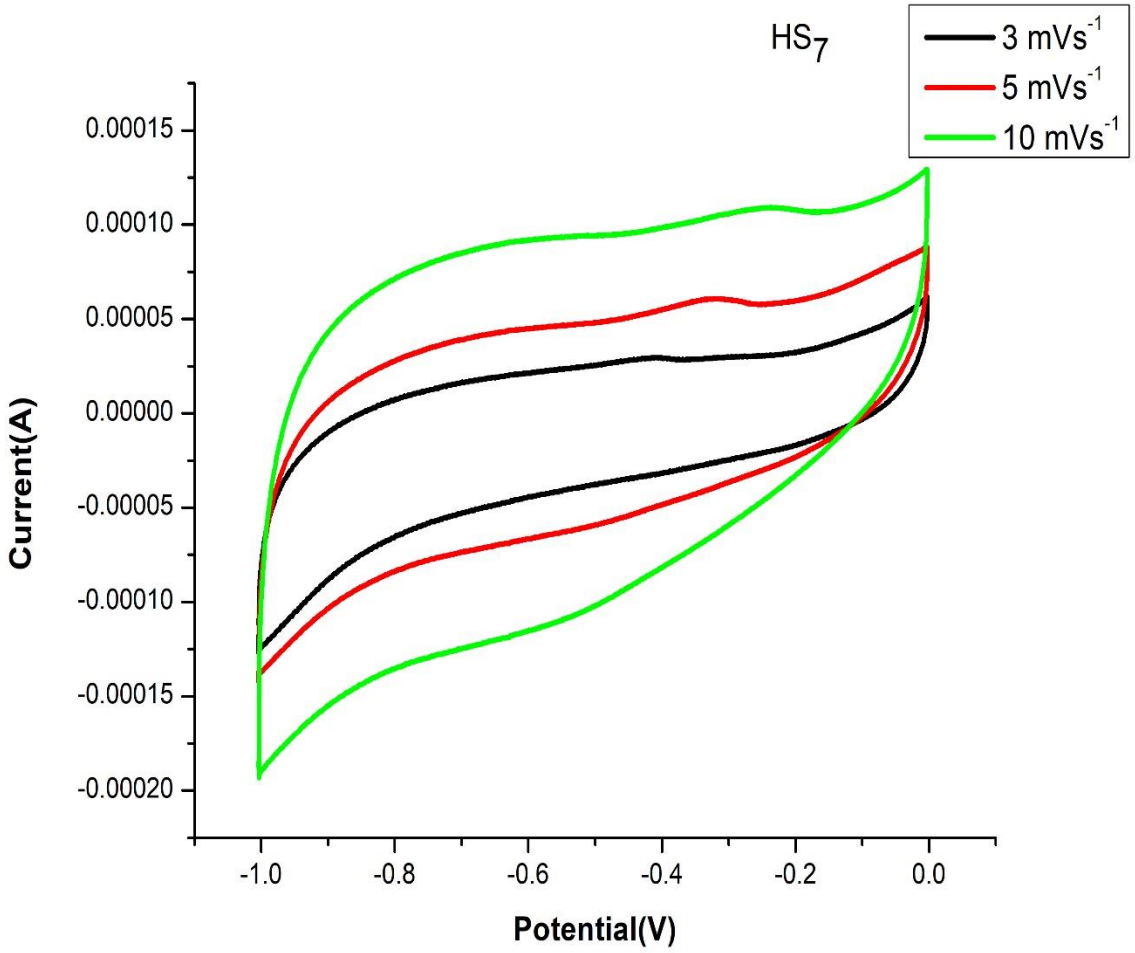

Figure 4.15: CV profile of prepared AC at 700^0C under KOH

The produced electrodes' CV curves at different scan rates, ranging from 3 mV/s to 10 mV/s, at 700 degrees Celsius. With different scan rates, such as 3 mV/s, 5 mV/s, and 10 mV/s, the electrode materials obtained an ideal rectangular form, as can be seen in the CV results.

Figure 4.16 shows the electrochemical behavior of the AC in the basic electrolyte.According to Figure 4.16: the CV profile of the activated carbon exhibits a rectangular form at various scanning rates. This Figure demonstrates how, within the specified voltage range, the AC electrodes behave as an electrical double layer capacitor.

The CV technique was used to examine the electrochemical stability of the AC electrode under basic electrolyte conditions for 100 cycles at a high scan rate of 20 mV/sec.

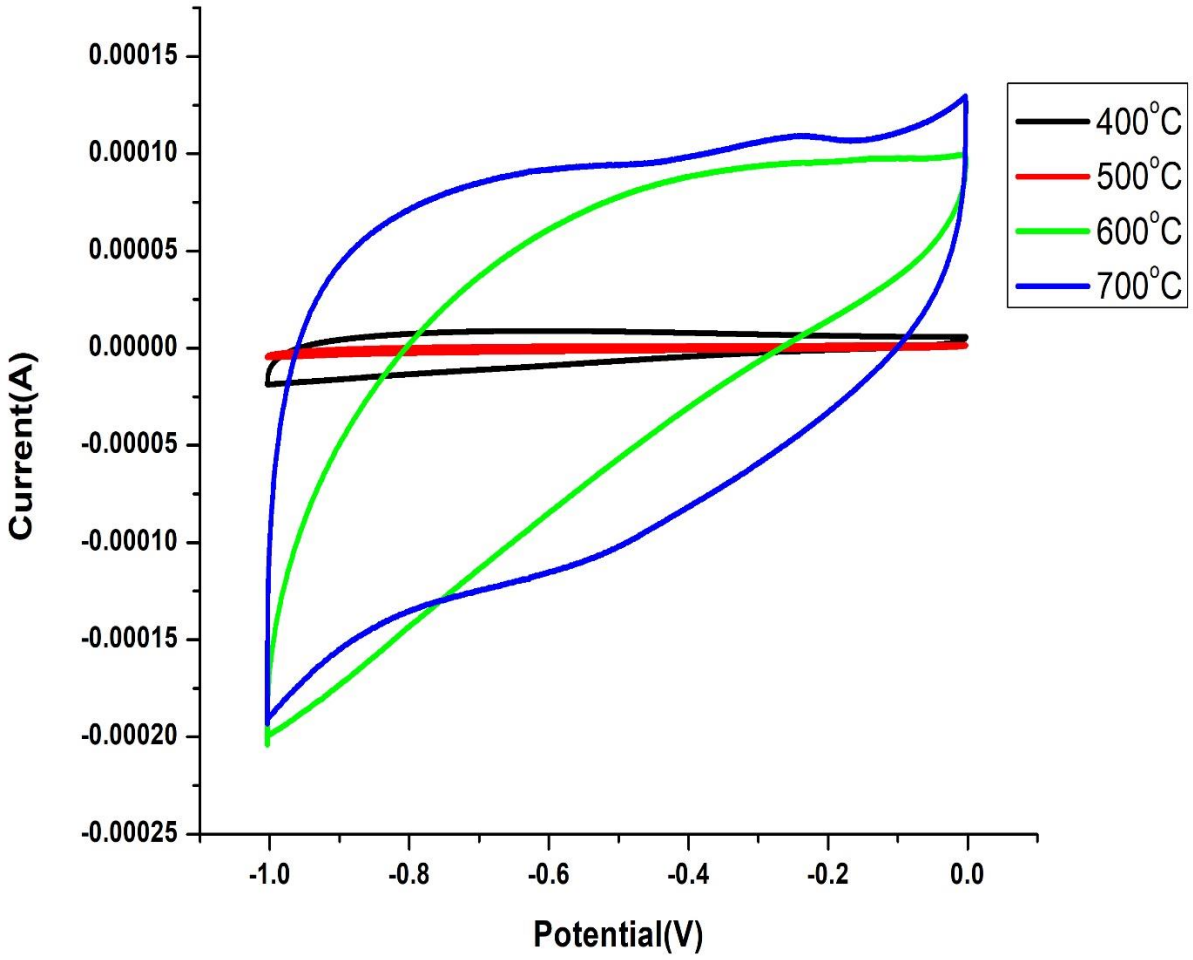

Figure 4.16: CV profile prepared AC at various temperatures under KOH

At different temperatures, such as 400^0C, 500^0C, 600^0C, and 700^0C, the specific capacitance of the measured electrode was 9.68×10^{-5} Fcm^{-1}, 1.414×10^{-6} Fcm^{-1}, 7.78×10^{-3} Fcm^{-1}, and 9.26×10^{-3} Fcm^{-1}, respectively. As temperatures increases, the loop area of the CV curve under the basic electrolyte increased. Sample HS_7 loop area was larger than that of the other samples in Figure 4.16.

The value of specific capacitance of prepared working electrode is good. So, it is appicable for energy storage devices. If the prepared AC is further altered by making it more conducive, that might then be employed as an electrode material for a supercapacitor.

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CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Harro seed stones were chemically activated using phosphoric acid in a 1:1 weight ratio at various carbonization tempreatures such as 400^0C, 500^0C, 600^0C and 700^0C for 4hrs to create high porosity activated carbon.The produced activated carbon (AC) were characterized by Methylene blue nubmer, Iodine number, SEM, Raman spectroscopy, Total pore volume, Surface area, Micro pore volume, XRD, FT-IR and CV. The prepared sample's surface area and iodine number at their greatest values were 960.46 mg/g and 977.19 m^2/g respectively at 400^0C for 4 hrs. Which is comparable to the commercial activated carbon (CAC).The greater value of Methylene blue number of the prepared sample was 334.72 mg/g at 700^0C for 4hrs. The surface area of prepared AC at 400^0C was more due to the value of Iodine Number. Surafce area is not the only ultimate parameter for electrode. For ion mobilization we used mesoporous activated carbon.Mesoporous activated carbon which helps in efficient ion transformation in between electrode and electrolyte.With the increase in carbonization tempreature, the OH group removed gradually in FT-IR spectra.Similarly, the sharp peak was gradually developed in the XRD graph, with increase in tempreature. Raman spetra shows that the prepared AC has semi-crystalline in nature. The specific capacitance of prepared AC electrode prepared at 700^0C was higher than other samples i.e. 2.96×10^{-3} Fcm^{-1}. Therefore, it is concluded that the prepared AC at 700^0C was good and it appears to be an effective sample fot the efficient ion transformation and it is applicable for energy storage devices.

5.2 Recommendations

The future enhancements for this research work are as follows:

- Using I_N and MB_N, the surface area of the prepared AC had been estimated. Future research may examine the prepared AC's BET surface area.
- Future studies are required to prepare AC from Harro stone utilizing KOH and $ZnCl_2$ as activators.
- It is possible to evaluate the influence of preparation factors like carbonization interval and impregnation ratio on the properties of AC.
- To produce more conductive activated carbon for application in high-performance energy storage devices, more study is necessary.

REFERENCES

Njewa, J.B., Vunain, E., & Biswick, T. (2022). Synthesis and characterization of activated carbons prepared from agro- wastes by chemical activation. Journal of chemistry, 9975444. https://doi.org/10.1155/2022/9975444

Ospino, J., Parra-Barraza, J.P., Cervera, S., Coral-Escobar, E.E., & Vargas-Ceballos, O.A., (2022). Activated carbon from cassava peel: A promising electrode material for supercapacitors. *Revista Facultad de Ingenieira Universidad de Antioquia*, (102), 88-95.https://doi.org/10.17533/udea.redin.20200803

Wei, B., Wei, T., Xie, C., Li, K.,& Hang, F. (2021).Promising activated carbon derived from sugarcane tip as electrode material for high- performance supercapacitos. *RSC advances*, 11(45), 28138-28147.DOI:10.1039/D1RA04143F

Maher, M., Hassan, S., Shoueir, K., Yousif, B., & Abo-Elsoud, M. E.A. (2021). Activated carbon electrode with promising specific capacitance based on potassium bromide redox additive electrolyte for supercapacitor application. J*ournal of Materials Research and Technology*, 11, 1232-1244. https://doi.org/10.1016/j.jmrt.2021.01.080

Mkungunugwa, T., Manhokwe, S., Chawafambira,A., & Shumba, M. (2021). Synthesis and characterization of activated carbon obtained from marula (Sclerocarya birrea) nut shell. *Journal of chemistry*. https://doi.org/10.1155/2021/5552224

Merin, P., jimmy Joy, P., Muralidharan, M.N., Veena Gopalan, E., & Semma, A**.** (2021). Biomass-derived activated carbon for high- performance supercapacitor electrode application. *Chemical Engineering & Technology*, 44(5), 844-851. https://doi.org/10.1002.ceat.202000450

Joshi, S., & K.C, B. (2020). Synthesis and characterization of sugarcane bagasse based activated carbon: Effect of impregnation ratio of $ZnCl_2$. *Journal of Nepal chemical society,* 41(1), 74-79.

Cheng, F., Yang, X., Zhang, S., & Lu, W. (2020). Boosting the supercapacitor performances of activated carbon with carbon nanomaterials. *Journal of Power Sources*, 450, 227678. https://doi.org/10.1016/j.jpowsour.2019.227678

Yaglikci, S., Gokce, Y., Yagmur, E., & Aktas, Z. (2020). The performance of sulphur doped activated carbon supercapacitors prepared from waste tea. *Environment Technology*, 41(1), 36-48. Doi.10.1080/095933302019.1575480

Saad, M.J., Sajab, M.S., Busu, W.N.W., Misran, S., Zakaria,S., Chin, S.X.,& Chia, C.H. (2020).Comparative adsorption mechanism of rice straw activated carbon activated with NaOH and KOH. *Sains Malasiana*, 49(11), 2721-2734.https://dx.doi.org/10.17576/jsm-2020-4911-11

Awasthi, G.P., Bhattarai, D.P., Maharjan, B., Kim, K.S., Park, C.H., & Kim, C.S., (2019).synthesis and characterizations of activated carbon from wisteria sinensis seeds biomass for energy storage applications. Journal of industrial and engineering chemistry, 72, 265-272.https://doi.org/10.1016/j.jiec.2018.12.027

Boujibar, O., Ghamouss, F., Ghosh, A., Achak, O., & Chafik, T. (2019). Activated carbon with exceptionally high surface area tailored nanoporosity obtained from nature anthracite and its use in supercapacitors. *Journal of Power sources*, 436, 226882. https://doi.org/10.1016/j.jpowsour. 2019.226882

Xie,Y.,& Zhou, Y.(2019).Enhanced capacitive performance of activated carbon paper electrode material. Journal of Material Research, 34(14), 2472-2481.https://doi.org/10.1557/jmr2019.224

Ahmed, S., Ahmed, A., & Rafat, M. (2018). Supercapacitor performance of activated carbon derived from rotten carrot in aqueous, organic and ionic liquid based electrolytes. *Journal of Saudi Chemical Society*, 22(8), 993-1002. https://doi.org/10.1016/j.jscs. 2018.03.002

Vijayakumar, M., Santhosh, R., Adduru, J., Rao, T. N., & Karthik, M. (2018). Activated carbon fibers as high performance supercapacitor electrodes with commercial level mass loading. *Carbon*, 140, 465-476. https://doi.org/10.1016/j.carbon. 2018.08.052

Joshi, S. (2017). Comparative study on the adsorption capacity of activated carbon prepared from lapsi seed stone and betel nut using phosphoric acid. Journal of the institute of engineering 13(1), 153-159.https://doi.org/10.3126/jie.v13il.20361

Laksaci, H., Khelifi, A., Trari, M., & Addoun, A. (2017). Synthesis and characterization of microporous activated carbon from coffee grounds using potassium hydroxides. *Journal of celeaner production*, 147, 254-262. https://doi.org/10.1016/j.jcepro. 2017.01.103

Ekpete, O.A., Marcus, A.C., & Osi, V. (2017). Preparation and characterization of activated carbon obtained from plantain (Musa paradisiaca) fruit stem. *Journal of chemistry,6.https://doi.org/10.1155/2017/8635625*

Shrestha, R.M. (2017). Characterization of Activated Carbons Prepared from a Locally Available Material by Iodine Number. *Journal of institute of engineering*, 13(1), 139-144.

Zhang, Y., Gao, Z., Song, N., & Li, X. (2016). High-performance supercapacitors and batteries derived from banana-peel with porous structure. *Electrochimica Acta*, 222, 1257-1266. https://doi.org/10.1016/j.electacta.2016.11.099

Joshi, S., Shrestha, L. K., Kamachi, Y., Malgras, V., Pradhananga, M. A., Pokhrel, B. P., Nakato, T., Pradhananga, R. R., Ariga, K., & Yamauchi, Y. (2015). Synthesis and characterizations of nanoporous carbon derived from Lapsi (Choerospondias axillaris) seed: Effect of carbonization conditions. *Advanced Power Techonology*, 26(3), 894-900. https://doi.org/10.1016/j.apt.2015.03.004

El- Sayad, G. O., Yehia, M. M., & Asaad, A. A. (2014). Assessment of activated carbon prepared from corncobby chemical activated with phosphoric acid. *Water Resources and industry*, 7-8, 66-75. https://doi.org/10.1016/j.wri.2014.10.001

Joshi, S., & Pokharel, B. P. (2013). Preparation and characterization of activated carbon from Lapsi (Choerospondias axillaris) seed stone by chemical activated with potassium hydroxide. *Journal of the Institute of Engineering*, 9(1), 79-88. https://doi.org/10.3126/jie.v9il.10673

Senthilkumar, S. T., Selvan, R. K., Lee, Y. S., & Melo, J. S. (2013). Electric double layer capacitor and its improved specific capacitance using redox additive electrolyte. *Journal of Materials Chemistry* A, 1(4), 1086-1095. https://doi.org/10.1039/C2TA00210H

Gottipati, R. (2012). Preparation and Characterization of microporous activated carbon from biomass and its application in the removal of chromium (VI) from aqueous phase. Department of Chemical Engineering. *Department of chemical Engineering National Institute of Technology, Rourkela Odisha, India, January, 1-242*

Liao, W.C., Liao,F.S., Tasai,C.T., & Yang, Y.P. (2012). Preparation of activated carbon for electric double layer capacitos. *China Steel Technical Report*, 25, 36-41.

Nunes, C. A., & Guerreiro, M.C. (2011). Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers. *Quimic Nova*, 34(3), 472-476. https://doi.org/10.1590/S0100-40422011000300020

APPENDIX A

Table A. 1: Calculation of I_N and MB_N of prepared AC at various temperatures.

AC Sample	Carbonization Temp. (1:1) ratio	Iodine number (mg/g)	Methylene Blue number (mg/g)
HS_4	400	960.45	331.3209
HS_5	500	914.53	266.1881
HS_6	600	851.53	325.3685
HS_7	700	880.38	334.7222
CAC	Commercial	929	378

Table A.2: Calculation of Surface Area, Micropore volume and Total pore volume of prepared AC at various temperature.

AC Sample	Carbonization Temp. (1:1) ratio	Surface area m^2/g	Total pore Volume Cm^3/g	Micro pore volume
HS_4	400	977.19	0.862	0.69
HS_5	500	878.48	0.734	0.48
HS_6	600	866.38	0.840	0.64
HS_7	700	901.49	0.861	0.68
CAC	Commercial	985	-	-

APPENDIX B

Figure B.1: Green Harro

Figure B.4: Harro seed stone powder

Figure B.2: Harro seed stone

Figure B.5: Phosphoric acid activation

Figure B.3: Sieving tool

Figure B.6: Carbonization

Figure B.7: Prepared AC

Figure B.10: Iodine Solution

Figure B.8: Washing AC with dil. Water

Figure B.11: Iodine number Test

Figure B.9: AC after washing and dried

Figure B.12: Methylene Blue Solution

Figure B. 13: Rotary Flask Shaker

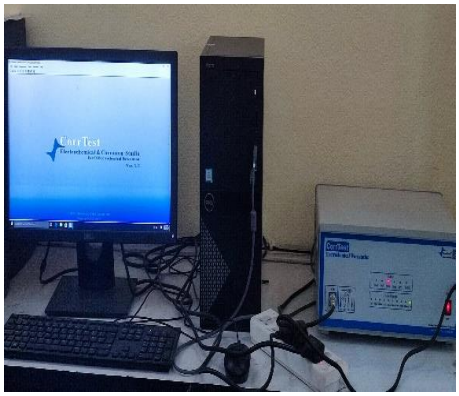

Figure B.16: Cyclic Voltamettry (Corr -Test) Electro chemical workstation) (5.5)

Figure B.14: MB_N Test

Figure B.17: PH meter

Figure B.15: UV/Vis (CEsI2-CE-100) spectrophotometer

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Date: September 20, 2022

To Whom It May Concern

This is to confirm that the paper titled "*Preparation and Characterization of Activated Carbon from Harro(Terminalia chebula)Seed Stone by Chemical Activation with Phosphoric Acid for energy storage devices*" submitted by **Kirti Bir Rajguru** with Conference ID **12371** has been accepted for presentation at the 12th IOE Graduate Conference being held in October 19 – 22, 2022 at Thapathali Campus, Kathmandu.

Khem Gyanwali, PhD
Convener,
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