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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

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**Abstract**
In order to meet the growing energy demand, low cost and effective energy storage devices are essential.In energy storage system, AC was applied as an electrode material.In this research work, activated carbons were derived from Harro (Terminalia chebula) seed stone by chemical activation with phosphoric acid in the ratio of 1:1 by weight at various temperatures such as 400℃ 500℃, 600℃ and 700℃.The prepared activated carbons(AC) was characterized by Methylene blue number, iodine number, surface area, total pore volume, FTIR and XRD. The electrochemical performance of prepared AC was studied as an electrode, in basic electrolyte. The highest value of Methylene blue number of prepared AC was 334.72 mg/g at 700℃ and the maximum surface area of prepared AC was 977.19 $m^2/g$ at 400℃ for 4 hrs.The CV profile of the prepared AC at 700℃ was ideally rectangular in shape and sample has mesoporous structure.Therefore, the AC prepared at 700℃ is applicable for energy storage devices.

**Keywords**
Activated Carbon, Phosphoric Acid, Electrode, Energy storage devices

## 1. Introduction

Activated carbon (AC) is a versatile group of adsorbents, with capability for selectively adsorbing carbonaceous solid materials resulting from bio-based materials.The term activated carbon refers to a family of thousands of inorganic and organic materials.The chemical bond and surface chemistry of prepared activated carbon depends on its chemical properties [1, 2, 3]. The activated carbon is characterized by a surface morphology, porosity, high surface area and electro-conducting amphoteric properties. The characteristics of ACs are influenced by chemical and physical properties of raw materials and activating agent [4]. Functional groups determine the general characteristics of the activated carbon such as hydrophobicity, polarization intensity, adsorption and acidity[5]. Activated carbons are prepared by the carbonization of the prepared carbon materials in the inert environment conditions via the activation of the carbon by using chemical activators. The technique of physical and chemical activation can be used to create activated carbon with a range of pore sizes.In terms of operational processes and mechanism, the development of porosity differs between the two ways.The production of activated carbon from Harro (Terminalia chebula) seed stones is useful for energy storage [1].

Supercapacitors can be recognized as a major energy storage devices. It is also known as electrochemical capacitors(ECs). Supercapacitors (SCs) are include pseudocapacitors and electrical double layer capacitors(EDLCs). In EDLCs,charges store electro optically through ion adsorption at the electrode-electrolyte interface. Two carbon-based electrode materials, sufficient electrolytes,and separator pseudocapacitors make up ELDCs,which use the Faradaic method to transfer charge loads electrostatically to store charges [1, 6]. Activated carbon provide improved performance as supercapacitors electrodes.It is mainly used in supercapacitor application than other form of carbon. AC has a more advantages such as low cost, high surface area and high porosity [7, 8, 9].

In present study, Harro (Terminalia chebula) seed stone was used as precursors for the preparation activated carbon(AC) because it is novel material and widely available in Nepal.

## 2. Material and Methods

### 2.1 Material

The Harro (Terminalia chebula) seed stones were collected from Naradevi 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 hours at 70°C. An electric grinder was used to compress the dry material.The crushed particles were sieved into a 300 micrometer size fraction.

### 2.2 Preparation of Activated Carbon

A series of 15g sample was mixed with 33ml of H3PO4 with impregnation ratio of 1:1 by weight and the mixed sample was stirred for 2 hours at 40°C. At this point, the slurry became black sticky solid. The impregnated sample was dried in an oven over night.The sample was placed in the quartz tube of length 60cm and internal diameter 3cm and inserted into the tubular furnace.The carbonization and activation were carried out at different temperature such as 400°C, 500°C, 600°C and 700°C under inert atmosphere. The product was cooled to room temperature. Then, the resulting carbons were dried in an electric oven at 100°C for 3 hours.

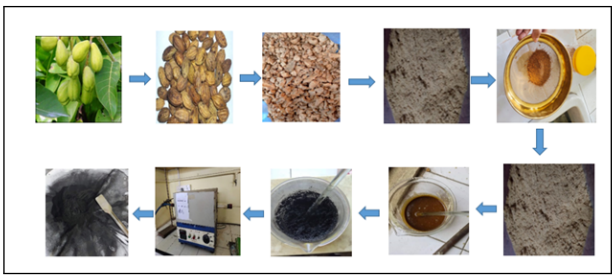

**Figure 1:** Process Block Diagram of preparation of Activated Carbon

### 2.3 Preparation of Activated Carbon (AC) Electrode

For the preparation of AC electrodes, Activated carbon powder, black carbon as 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 micro lit.) and then dried at 50°C for 1 hr and 100°C for 2 hrs.

### 2.4 Characterization of Activated Carbon

#### 2.4.1 Electrochemical characterization

Supercapacitors, often referred to as EDLCs, are a key power source for digital communications, memory backups, and electric vehicles due to their long cycle life and high power density.Two carbon electrodes separated by the electrolyte are frequently used in the production of EDLC devices. The non-faradaic reaction and capacitive behavior of the EDLC can be highlighted by employing a suitable technique, such as cyclic voltammetry (CV).

The electrochemical properties the prepared carbon electrodes were investigation by the three electrode system.The reference electrode (Ag/AgCl), counter electrode, and working electrodes make up the three electrodes system.The cyclic voltammetry (CV) performed in 4M KOH electrolyte. The capacitive activity of prepared AC electrodes was detect by using CorrTest Electrochemical workstation (5.5). The basic solution KOH is an useful electrolyte for energy storage applications, as shown by the symmetrical I-E response curves, which exhibit good capacitive responses over the examined potential range.CV measurements were taken at various sample rates ranging from 3 to 20 mV/s using a potential window from 0 to -1V. [6, 7, 10, 11].

#### 2.4.2 Yield Analysis of activated carbon

The yield of prepared activated carbon was calculated by using following formula:

$$Yield(\%) = (w2/w1)100\% \quad (1)$$

Where w1 is the mass of the Harro powder and w2 is the mass of the prepared activated carbon.

#### 2.4.3 Iodine Number

The degree of micro pore distribution in the activated carbon is depicted by the iodine number.The milligram of iodine that is absorbed by a gram of activated carbon is known as the iodine number.An accurate estimation of the surface area and micropore concentration of activated carbon is provided by the iodine number.The iodine number can be calculated as:

$$IodineNumber(mg/g) = C * ConversionFactor(C.F) \quad (2)$$

where, C is the difference between Blank Reading and Volume of hypo solution consumed by adsorption of

hypo solution by activated carbon. The Conversion Factor(C.F) is determined from the equation as

$$C.F = \frac{Eq.weight of Iodine \times Normality of Iodine \times 10}{Wt.of Activated carbon \times Blank reading} \quad (3)$$

where, Blank reading = the volume of standard hypo solution needed to determine the prepared iodine solution.[12]

#### 2.4.4 Methylene blue number

The degree of meso pore distribution in the activated carbon is depicted by the methylene blue number. In this process, 75ml of solution were in encounter with 0.1 gram of activated carbon(AC). Methylene blue solution of concentration 75mg/L for 3 hours at room temperature followed by intermittent shaking using electric shaker (Digital VDRL Rotatory –RPM-s). The solution was thereafter filtered and the remaining concentration of Methylene blue.The process of determination of Methylene blue number in mg/g is given below:

$$Methylenebluenumber(mg/g) = [(Co - Ce) * V]/M \quad (4)$$

Where, M is the mass of the activated carbon in grams(g), V is the volume of the solution in liters, Co is the initial concentration (mg/L), Ce is the equilibrium concentration (mg/L).[12]

#### 2.4.5 Surface Area

The surface area of activated carbon was calculated using a multiple regression equation using the values of the iodine number and Methylene blue number. The surface area of prepared activated carbon (AC) can be determined using the equation below: [12]

$$\begin{aligned} \mathrm{S}\left(\mathrm{m}^2\ \mathrm{g}^{-1}\right) = {} & 2.28 \times 10^2 - 1.01 \times 10^{-1}\mathrm{MBN} + 3.00 \\ & \times 10^{-1}\mathrm{IN} + 1.05 \times 10^{-4}\mathrm{MBN}^2 + 2.00 \\ & \times 10^{4}\mathrm{IN}^2 + 9.38 \times 10^{-4}\mathrm{MBN} \times \mathrm{IN}) \end{aligned} \quad (5)$$

#### 2.4.6 Total Pore Volume

A multiple regression equation was utilized to determine the Total pore volume of activated carbon using the value of iodine number and Methylene blue number. The following equation can be used to determine the Total pore volume:[12]

$$\begin{aligned} &\text{Total Pore Volume}\left(\mathrm{cm}^3\ \mathrm{g}^{-1}\right) \\ &= 1.37 \times 10^{-1} + 1.90 \times 10^{-3} MBN + 1.00 \times 10^{-4} IN \end{aligned} \quad (6)$$

#### 2.4.7 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was used to examine the surface chemistry of the AC samples created for this investigation.The percentage of transmission of sample was recorded over 500-4000 Cm-1. FTIR spectra for all sample were recorded using SHIMADZU Spectrophotometer, Department of Plant Resources Nepal.

#### 2.4.8 X-ray Diffraction (XRD)

The prepared activated carbon from Harro (Terminalia chebula) seed stone were homogeneously spread on the surface of a glass slide and mounted on Beaker D2 Phaser X-ray Diffractometer, NAST Nepal.

## 3. Results and Discussion

By chemically activating Harro (Terminalia chebula) seed stones with phosphoric acid, activated carbon was created. Several techniques, including yield analysis, iodine number, Methylene blue number, surface area, Total pore volume, FTIR, XRD, and CV, were used to estimate the amount of obtained activated carbon. The effect of various carbonization temperature and Harro seed stones powder with phosphoric acid were studied.

### 3.1 Yield Analysis of Activated Carbon

The yield of the different samples by the method of chemical activation with phosphoric acid at different temperatures are summarized in Figure 2.

As shown in Figure 2, the yields of activated carbon obtained from Harro seed stones were in the range of (31.73 – 45.53)% at various temperatures.

The activated temperature plays an important role in the yield of activated carbon, Fig.2: shows that, the carbon yield decreased from 45.53% at 400°C to 31.73% at 700°C, due to the aromatic condensation reaction that result in the evolution of gaseous products from the hydro-aromatic structure of carbonized product and this led to an increased release of volatile matters.

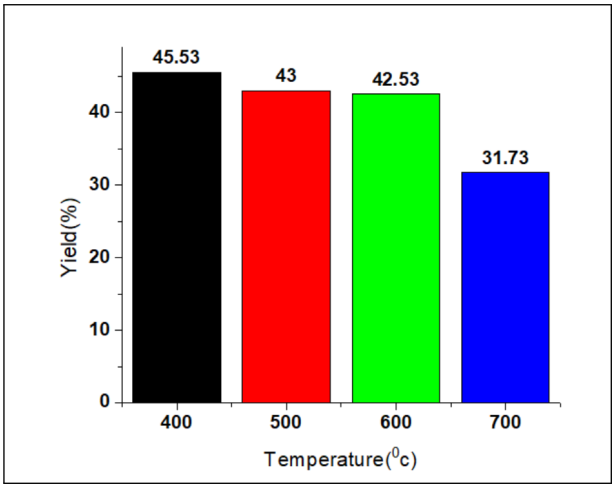


**Figure 2:** Effect of carbonization temperatures on the yield analysis of the phosphoric Acid activated carbon

### 3.2 Iodine number and Methylene blue number

A quick and easy test technique for determining the porosity structure of micro carbons is the iodine number test method. It may enter the prepared activated carbon's deep micropores despite its tiny molecular size. Iodine number therefore provides an approximation of the micropore count in the produced AC. Iodine number is often employed as an indication for the adsorbent and porosity of the activated carbon in order to calculate its surface area.[1, 2] The remaining variables are maintained constant by the variation in the activated carbon iodine number as a function of carbonization temperature.

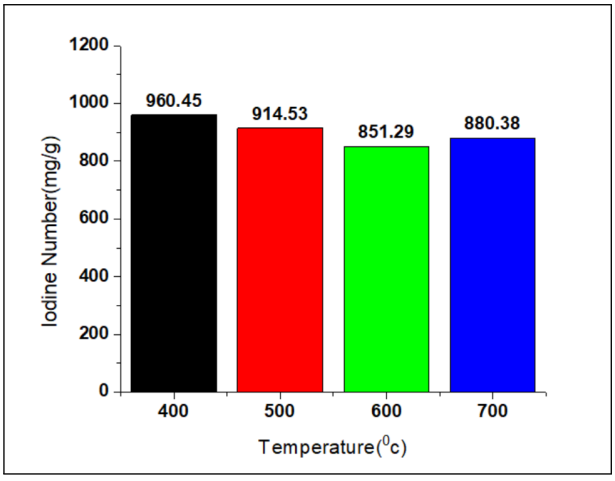


**Figure 3:** Effects of carbonization temperatures on the iodine number of phosphoric Acid activated carbon

We can observe from Figure 3: The iodine value grows till a temperature of 600°C. Iodine number provides a rough estimation of pore content.These results indicate that the carbonization temperature has a significant role in the pore structure of activated carbon.The proliferation of mesopores may be the cause of the reduction in iodine number with rising carbonization temperatures. [1, 2, 5].

Methylene blue number test is one of the easy and fast test method for evaluating the porous structure of Activated carbon.The Methylene blue number represents the distribution of mesopores in the prepared activated carbon,which also reveals how well the carbon can transfer ions. Methylene blue number characterization is mainly done for the purpose of obtaining the information on creation of mesopore structure on the prepared activated carbon. Methylene blue number is also used to calculate the surface area and Total pore volume. [2, 3]

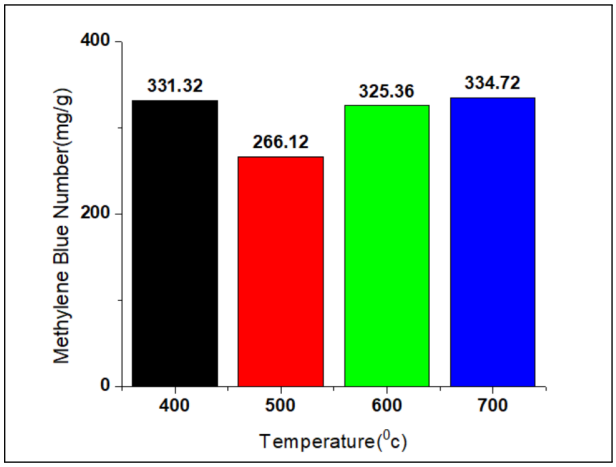


**Figure 4:** Effect of carbonization temperatures on the Methylene blue number of the phosphoric Acid activated carbon

The Methylene blue number of activated carbon prepared from Harro seed stone powder of different temperatures 400°C, 500°C, 600°C and 700°C were 331. 32 mg/g, 266.12 mg/g, 325.36 mg/g and 334.72 mg/g respectively as shown in Fig:4. The value of Methylene blue number were decreasing with temperatures upto 600°C and increased at 700°C due to the creation of mesopores and such type of mesoporous activated carbon helps in efficient transfer of ions.

### 3.3 Surface Area

The physical structure properties of activated carbon prepared from Harro seed stones with at different

temperatures as shown in Figure 5: The surface area of activated carbon prepared from Harro seed stones powder at different temperatures 400°C, 500°C, 600°C and 700°C were 977.19 $m^2$/g, 878.48 $m^2$/g, 866.49 $m^2$/g and 977.19 $m^2$/g respectively.[5]

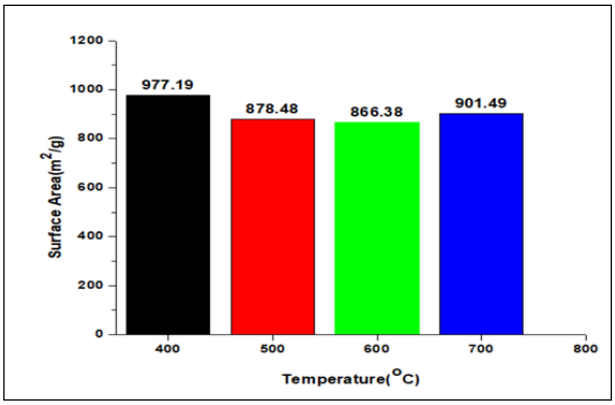


**Figure 5:** Effect of carbonization temperatures on the surface area of the phosphoric Acid activated carbon

## 3.4 Total pore volume

The total pore volume prepared AC was determine by using iodine number and Methylene blue number.The total pore volume of activated carbon prepared from Harro seed stones powder at different temperatures 400°C, 500°C, 600°C and 700°C were 0.862 $cm^3/g$, 0.734 $cm^3/g$, 0.84 $cm^3/g$ and 0.862 $cm^3/g$ respectively. which is shown in Figure 6: [5]

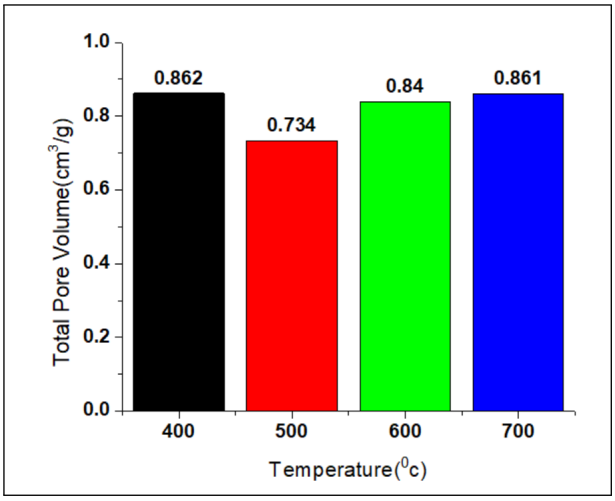


**Figure 6:** Effect of carbonization temperatures on the Total Pore Volume of the phosphoric Acid acitivated carbon

## 3.5 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform-Infrared (FTIR) Spectroscopy was used to detect the surface functional groups of the prepared activated carbon from Harro seed stones Figure 7 Shows FTIR spectra of the synthesis carbons obtained by phosphoric acid activated at different carbonization temperatures [3, 5].

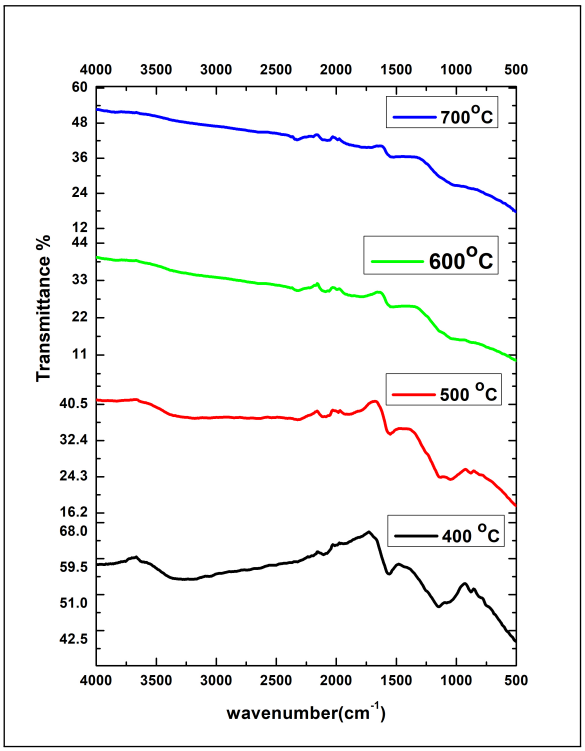


**Figure 7:** FTIR spectrum of prepared AC from Harro seed stones at various carbonization temperature

The bands at 879.54 $cm^{-1}$ in the FTIR spectrum of the synthetic activated carbons prepared at 400°C and 500°C were caused by out of plane deformation of C-H for various substituted benzene rings. The prepared AC's FTIR spectra exhibited three main absorption bands at 1527.62 $cm^{-1}$,1550.77 $cm^{-1}$ and 1558.48 $cm^{-1}$. Additionally, the aromatic ring often present in carbon materials' aromatic rings exhibits C=C stretching vibrations, which cause the absorption peak of different samples prepared at 400°C, 500°C, 600°C and 700°C to be at roughly 1558.48 $cm^{-1}$,1550.77 $cm^{-1}$,1558.48 $cm^{-1}$and 1527.62 $cm^{-1}$ respectively. FTIR spectrum of the prepared sample at 400°C, the broad peak observed at 3278.99 $cm^{-1}$ due to the presences of -OH stretch group. Similarly, In FTIR spectrum of the prepared samples at 600°C and 700°C indicates there is removal of -OH group due to dehydration [3, 5].

### 3.6 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) helps to determine the crystal structure of the prepared AC samples.The XRD pattern of the activated carbon (AC) prepared from Harro seed stones at various carbonization temperatures are shown in Figure 8:

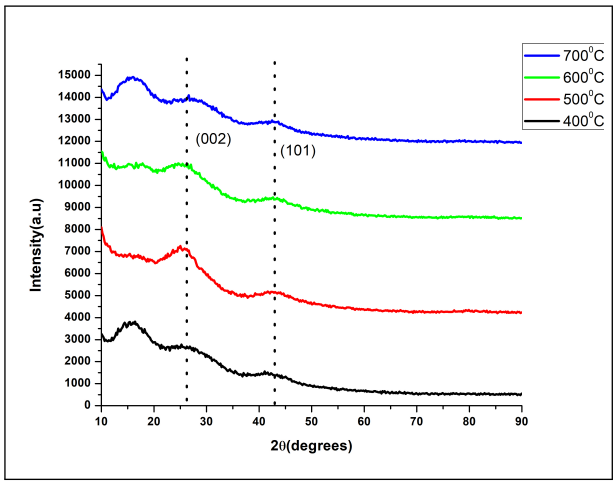


**Figure 8:** XRD pattern of prepared AC from Harro seed stones at various carbonization temperatures

X-Ray diffraction (XRD) is mainly done for the identification of diffraction pattern and phase orientation of prepared sample.The XRD patterns of prepared Activated carbon at various carbonization temperatures such as 400°C, 500°C 600°C and 700°C as shown in Figure 8:The XRD patterns of AC prepared at 400°C, and 700°C were very similar and also the XRD patterns of AC prepared at 500°C,and 600°C very similar.All sample showed slightly sharp peaks at 25.8 degree and 42.5 degree respectively.The sample prepared at 500°C and 700°C show sharp peaks at (002) diffraction at 25.8 and (101) diffraction at 42.5, indicating the crystalline nature of prepared activated carbon.As the carbonization temperature increases, the peaks of the prepared activated carbon slightly sharpens that indicates the more ordered structure of the prepared sample [13, 14].

### 3.7 Electrochemical performance of AC under Basic Electrolyte

The electrochemical behavior of the prepared samples was evaluated using a three electrodes system in 4M KOH electrolyte.The electrochemical performance of AC in the basic electrolyte is depicted in Figure 9: The CV technique was used to test the cycle stability of the AC electrode in a basic electrolyte over 20 cycles at a high scanning rate of 20 mV$s^{-1}$.The CV profile of the activated carbon prepared at various temperatures such as 400°C, 500°C, 600°C and 700°C as shown in Figure 9: and exhibits a rectangular form at same scan rate [7, 14].

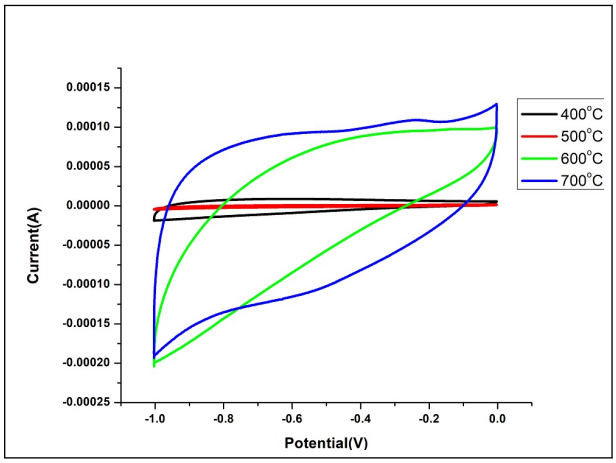


**Figure 9:** Current potential curve of phosphoric acid activated AC of different samples at various temperatures under basic electrolyte at scan rate 10 mVs-1

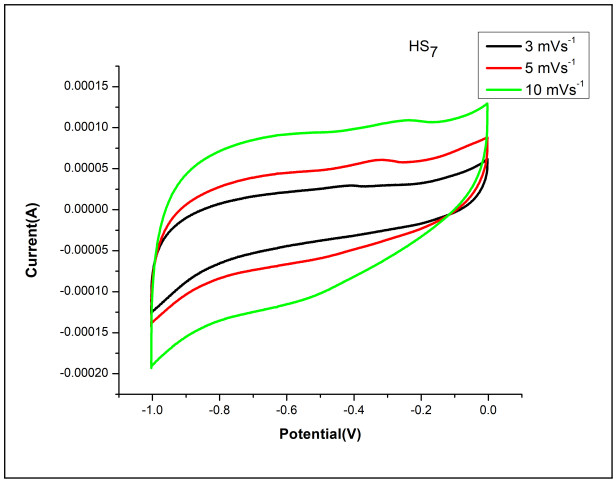


**Figure 10:** CV curve of prepared AC at 700°C

Figure 10 Shows the CV curve of the prepared activated carbon at 700°C at different scan rates such as 3 mV$s^{-1}$,5 mV$s^{-1}$and 10 mV$s^{-1}$.The sample prepared at 700°C, it was reported that an ideal rectangular shape and the CV curve do not reveal any sharp and distinguishable peaks.This figure demonstrates how, with in the specified potential range, the AC electrodes behave as an electrical double layer capacitor.

## 4. Conclusion

Harro (Terminalia chebula) seed stones were chemically activated using phosphoric acid in a 1:1 weight ratio at various carbonization temperatures, such as 400°C, 500°C, 600°C and 700°C for 4 hrs to produce highly porous activated carbon.The produced AC were characterized by Methylene blue number, iodine number, surface area, Total pore volume, XRD, FTIR, and CV.Iodine number and Methylene blue number were used to calculate surface area and Total pore volume of the prepared samples.The highest value of iodine number was found to be 960.46 mg/g at 400°C and the highest value of Methylene blue number of the prepared sample was 334.72 mg/g at 700°C. Which is comparable to the commercial activated carbon (CAC). The maximum surface area of 977.19 $m^2$/g was obtained from Harro seed stone carbonized at 400°C for 4 hrs. Surface area of prepared activated carbon at 400°C, was high due to the value of iodine number. The surface area and iodine number of prepared AC at 400°C were more but Surface area is not the only ultimate parameter for electrode. For ion mobilization we need mesoporous activated carbon (AC). Mesopore structure of the prepared activated carbon which helps in efficient ion transformation in between electrode and electrolyte. With the increases of carbonization temperature, the -OH group removed gradually in FTIR spectra.Similarly, the sharp peak was gradually develop in the XRD graph with increase in temperature. The CV profile of the prepared sample at 700°C was ideally rectangular. Therefore, it is concluded that the AC prepared at 700°C was good and it appears to be an effective sample for the efficient ion transformation and it is applicable for energy storage devices. The synthesis of activated carbon and potential uses for it in energy storage devices are the major issues addressed in this research work. The research has so far been carried out with the minimum laboratory resources available. The recommendations from this study are as follows:

1. The surface area of the prepared AC had been calculated by using IN and MBN. Future research may examine the prepared AC's BET surface area.

2. Future studies are required to prepared AC from Harro seed stone utilizing KOH and ZnCl2 as an activators.

3. To evaluate the specific capacitance of the prepared AC.

4. To produce more conductive activated carbon for application in high performance energy devices, more study is necessary.

## 5. Acknowledgement

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