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Preparation and Characterization of Activated Carbon from Amla (Phyllanthus emblica)Seed Stone by Chemical Activation with Phosphoric Acid for Energy Storage Devices

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Abstract
In order to mitigate climate change and ensure stable energy supply, storage of renewable energy is indispensable. Activated carbon (AC) has a large surface area which makes it ideal electrode for energy storage devices such as supercapacitors. In this work, we have used Amla seeds as precursors to produce AC because of their novelty and to manage agricultural waste produced by the seeds. The AC was produced at temperatures of 400℃, 500℃ and 600℃ using Phosphoric acid as activating agent. Their characterization showed AC prepared at 500 ℃ had high porosity and was thus suitable for the electrode of the supercapacitor. The voltagramm of the the 500 ℃was nearly rectangular which showed that the synthesized material is a porous AC.

Keywords
Activated Carbon, Electrode, Energy Storage

1. Introduction

While non-renewable energy sources like fossil fuels are harmful to human health as well as the environment, renewable energy is challenged by the inability to provide a constant energy supply[1]. This makes energy storage a necessity.

It is possible to store energy in several ways, such as batteries, capacitors, etc. Each has its own advantages as well as disadvantages. The Supercapacitors(SCs) are energy storage device that combine high energy storage density with very high power density. SCs are not a substitute for batteries, but rather an additional form of energy storage. Supercapacitors store energy by dispersing charged ions in the electrolyte on the electrode surfaces[2].

Electrical double-layer capacitors(EDLCs) are a type of SC which can accumulate ions electrostatically on porous electrode surface. The most used material in the form of active material in commercial EDLCs is Carbon.A unique mix of easy availability,low to moderate cost,good conductivity and extremely high surface area makes activated carbon(AC) incomparable to other electrode materials[3].

Pores in AC range from visible to nanometer dimensions. According to the IUPAC (International Union of Pure and Applied Chemistry), three groups of pores are distinguished, according to the pore size:

- Macropores ($>$ 50 nm diameter)
- Mesopores (2-50 nm diameter)
- Micropores ($>$ 2 nm diameter) [4]

The porous activated carbon can be produced by physical or chemical activation[5]. Physical activation generally requires high temperature hence we used chemical activation using phosphoric acid for the AC synthesis[6]. When AC is used as an electrode in a supercapacitor, there is more area for the exchange of ions, electrons, etc, and hence more current can flow.

There are many studies to prepare activated carbon using a precursor of biomass of wheat, corn straw, olive stones, Lapsi seeds, etc [4].This research aims to use a locally abundant novel biomass-based precursor of amla seeds native to our area and activated using easily available phosphoric acid.Though the application of AC is diverse, we will use it as an electrode for energy storage applications for the purpose of this research.

2. Materials and Methods

2.1 Chemicals and Reagents

The following chemicals were used in the research work : Phosphoric Acid (H_3PO_4) from Finar India,Iodine from Thermo Fisher Scientifc India, Potassium Iodide(KI) from Merk (India),Potassium dichromate ($K_2Cr_2O_7$) from Fisher Scientific, Sodium Thiosulphate ($Na_2S_2O_3.5H_2O$) from Fizmerck India, Potassium hydroxide (KOH) from Fizmerck India, Sulphuric acid (H_2SO_4) from Fisher Scientific, Hydrochloric acid (HCl) from Fisher Scientific.

The reagents prepared for the research work were :

1. Methylene Blue Solution
2. 0.1N Iodine Solution
3. 5 percent HCL
4. 0.1M Sodium thiosulphate
5. 1 percent Starch

2.2 Instruments

The following instruments were used in the entire experimental work:Horizontal tubular furnace,Spectrophotometer,pH meter,Electric shaker,X-ray diffractometer,Fourier Transform-Infrared (FTIR) Spectrometer, Cyclic Voltameter.

2.3 Preparation of Activated Carbon

Amla stones brought from the local market were washed with distilled water until significant amount of impurities were removed. The washed stones were dried in the electric oven for 24 hours at 100° C. The dry stones were ground and the resulting powder precursor was sieved to get a particle size of 250 µm. 15 gm of the precursor and 33 ml of Phosphoric Acid were mixed in a beaker resulting in an impregnation ratio of 1:1 and stirred until the powder was wet completely. The mixture was placed inside an oven at 70° C for 24 hours. The obtained product was kept inside the middle of a quartz tube. The tube was transferred to a horizontal tubular electric furnace and carbonized at 400°C (S_{400}) , 500°C (S_{500}), and 600°C (S_{600}) under a continuous flow of nitrogen gas at a flow rate of 100 ml/min, for 4 hrs. The prepared sample was washed with distilled water until the pH of the filtrate reached a value between 6.5 and 7. It was then dried in the oven for 3 hours at 110°C. The characterization and electrochemical analysis were performed after the synthesis of activated carbon. The flowchart of the experimental work is as shown in the figure:

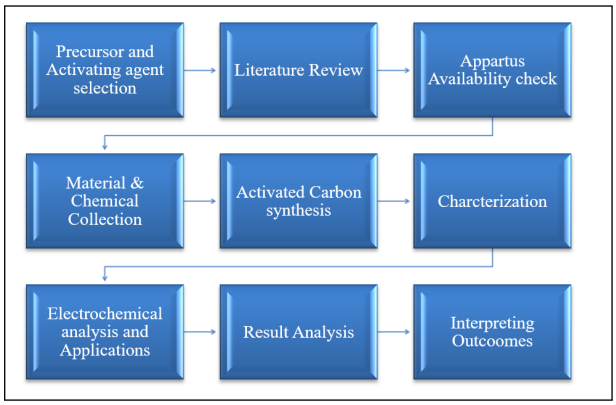

Figure 1: Preparation and Characterization of AC

2.4 Characterization of Activated Carbon

2.4.1 X-ray diffraction

The prepared activated carbon from Amla (Phyllanthus Emblica) seed stone were homogeneously spread on the surface of a glass slide and mounted on Beaker D 2 Phaser X-ray Diffractometer, NAST, Nepal.To further calculate the crystallite size we use Scherrer's equation as follows:

$$B = \frac{0.9 \times \lambda}{d \times \cos\theta} \tag{1}$$

where

d: Full Width at Half Maximum (FWHM) intensity of the peak (rad) [7].

2.4.2 Fourier Transform- Infrared (FTIR) Spectroscopy

The presence of functional groups and fingerprint of the sample was investigated using FTIR spectroscopy[8]. The percentage 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.

2.4.3 Iodine Number

Iodine number is the milligram of iodine adsorbed by one gram of carbon[4]. Iodine number gives a good approximation of the surface area and micropore

content of Activated Carbon. The iodine number was determined according to the standard method [9].

The Iodine Number can be calculated as:

$$\text{Iodine Number}(mg/g) = C \times \text{Conversion Factor} \quad (2)$$

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

$$C.F = \frac{\text{Eq. weight of Iodine} \times \text{Normality of Iodine} \times 10}{\text{Weight of AC} \times \text{Blank reading}} \quad (3)$$

where,
Blank reading = the volume of standard hypo solution needed to determine the prepared iodine solution strength[10].

2.4.4 Methylene blue adsorption

Methylene Blue is a synthetic amorphous dye. It is dark green powder but in the aqueous form, it is blue in color. In water, it decomposes into Methylene Blue cation and chloride ion.

Methylene blue number(MBN) gives the amount of methylene blue dye adsorbed by 1 gram of adsorbent which is activated carbon. MBN was determined by the single-point isotherm method in this research paper.

$$MB(mg/g) = \frac{(Co - Ce) \times Ve}{M} \quad (4)$$

Where,
C_o = initial concentration of MB solution (mg/L)
C_e = equilibrium concentration of MB solution (mg/L)
Ve = volume of adsorbate solution in liter & m = mass of adsorbent in gram(g) [11]

2.4.5 Surface Area

The surface area of activated carbon was determined by multiple regressions model using the iodine number and methylene blue numbers [9].

2.4.6 Total Pore Volume

The total pore volume of the sample is determined by the linear model through multiple regressions method[9].

$$Vt_{(\text{cm}^3\ \text{g}^{-1})} = 1.37 \times 10^{-1} + 1.90 \times 10^{-3} MBN + 1.00 \times 10^{-4} IN \quad (5)$$

2.4.7 Micropore Volume

The micropore volume of the activated carbon can also be estimated through methylene blue number and iodine number by multiple regression method[9].

$$Vm_{(\text{cm}^3 g^{-1})} = 5.60 \times 10^{-2} - 1.00 \times 10^{-3}\text{MBN} + 1.55 \times 10^{-4} IN + 7.00 \times 10^{-6}\text{MBN}^2 + 1.00 \times 10^{-7} IN^2 - 1.18 \times 10^{-7}\text{MBN}IN \quad (6)$$

2.4.8 Preparation of Electrode

For the electrode, 4 mg of AC is taken. Prepared activated carbon, carbon black and polyvinylidene difluoride (PVDF) are mixed in the ratio of 8:1:1 by weight in isopropyl alcohol to form a homogeneous mixture. This mixture is coated in a glassy carbon electrode uniformly. The coated mixture was dried for 6 h and the electrode was prepared [12].

2.4.9 Electrochemical Analysis of AC

Cyclic Voltammetry : For the Cyclic Voltammetry process, we use 3 electrode system. It consists of a working electrode, a reference electrode, and a counter electrode. Silver-Siver chloride is used as a reference electrode, Platinum wire is used as a counter electrode and glassy carbon or our prepared electrode is used as a working electrode. A basic electrolyte solution of 6M KOH was prepared and put in the cell. [13]

3. Results and Discussion

The following table gives all the information about the characterization results of AC.

Sample	MB_N	Iodine Number	Surface Area	Meso pore Volume	Total Pore Volume
S_{400}	249	750.43	722.39	0.39	0.68
S_{500}	307	842.58	844.28	0.57	0.81
S_{600}	291	831.42	822.12	0.53	0.77

3.1 Methylene Blue Adsorption

Methylene Blue Number gives information regarding mesopore distribution of AC. As shown in the graph below, the (S_{500}) sample of AC prepared at 500° C had a better mesopore distribution compared to the other two samples.

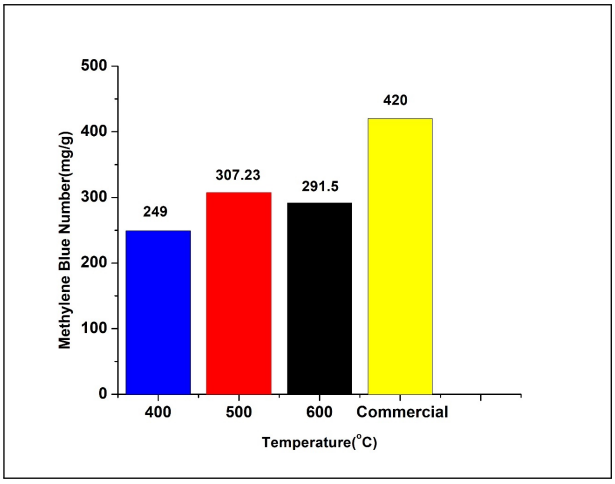

Figure 2: Methylene Blue Number of three ACs

3.2 Iodine Number

Iodine Number gives information regarding micropore distribution of AC. As shown in the graph below, the ($S_5$00) sample of AC prepared at 500° C had a better micropore distribution compared to the other two samples.

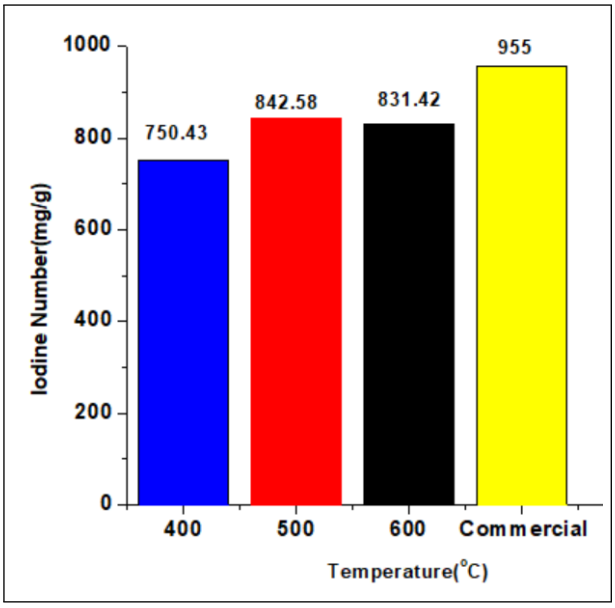

Figure 3: Iodine Number of three ACs

3.3 X-Ray Diffraction

The figure shows the X-ray diffraction patterns of the activated carbon prepared at 400°C,500°C, and 600°C. The peaks centered at around 26 and 42 degrees correspond to the (002) and (001) planes. It shows that the Activated Carbon is composed of graphite crystallites.

The crystallite size for the samples (S_{400}),(S_{500}),(S_{600}) was found using Scherrer equation to be 21.5 nm,9.505 nm, and 13.207 nm.

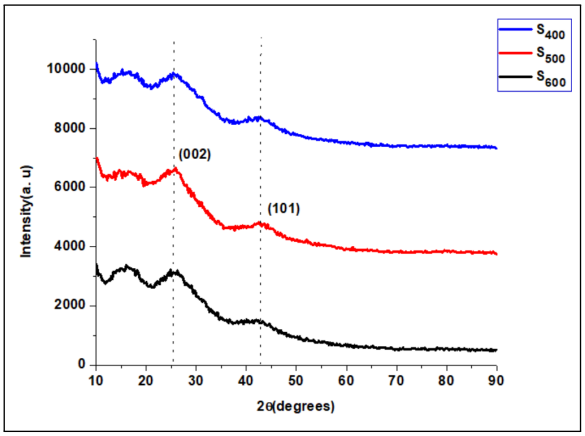

Figure 4: XRD pattern of three ACs

3.4 Fourier Transform-Infrared(FTIR)

Fourier Transform-Infrared (FTIR) Spectroscopy was used to detect the surface functional groups of the prepared activated carbon from Amla seed stones. FTIR spectra of the prepared AC showed the major absorption band at 1056 (cm^{-1})and 2952 (cm^{-1}) respectively due to C=C stretching vibrations in the aromatic ring commonly found in the carbon materials.

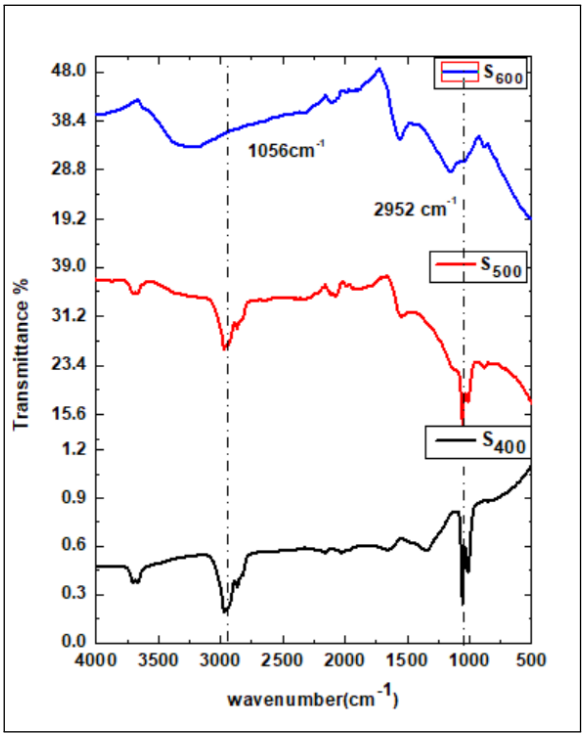

Figure 5: FTIR Spectroscopy of three ACs

As the temperature of activation is increased the - OH

functional group disappears as it's peak is shown to decrease and continiously disappear as in sample (S_{600}) which is at temperature 600 degrees.

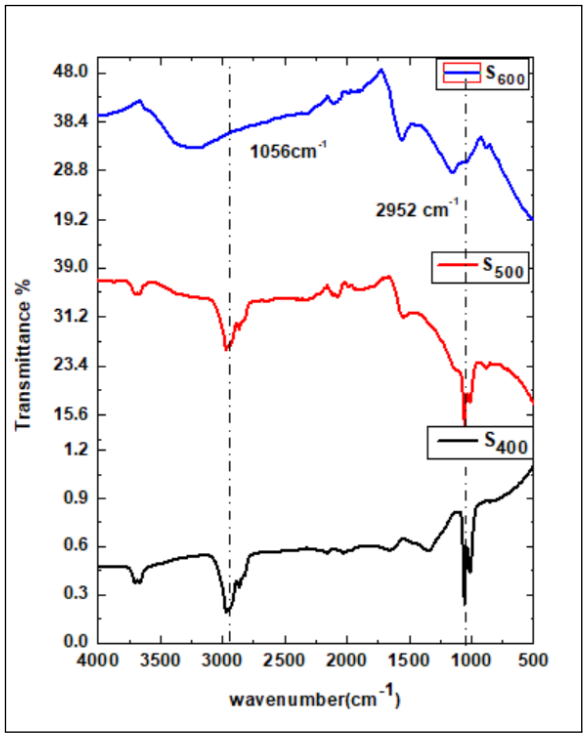

Figure 6: FTIR Spectroscopy of three ACs

3.5 Surface Area

The figure shows surface area of the AC at different temperature. The surface area varies from 722 to 844 m^2gm^{-1}.

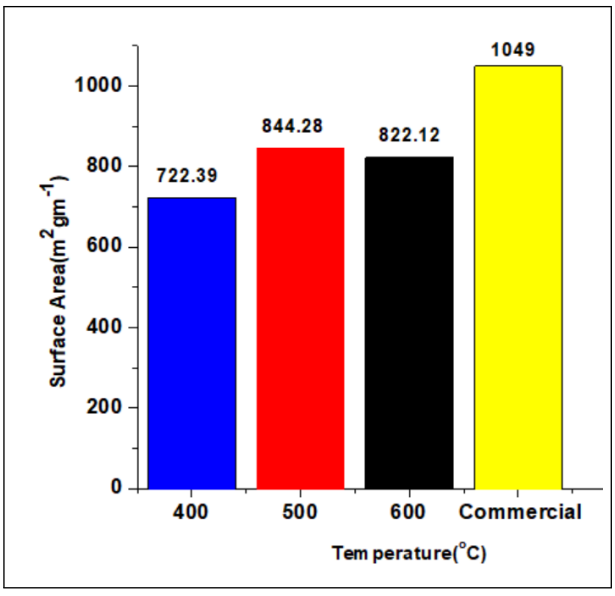

Figure 7: Surface Area of three ACs

3.6 Micropore Volume

The figure shows the micropore volume of the AC at different temperature. The micropore volume varies from 0.39 to 0.57 cm^3gm^{-1}.

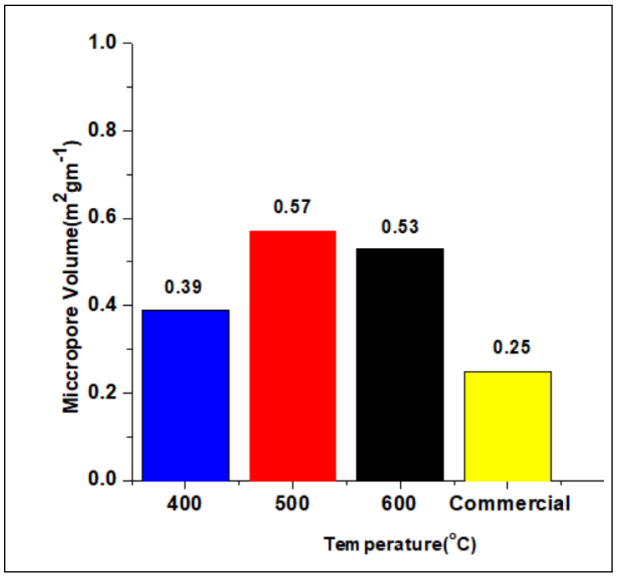

Figure 8: Micropore Volume of three ACs

3.7 Total Pore Volume

The figure shows total pore volume of the AC at different temperature. The total pore volume varies from 0.68 to 0.81 cm^3gm^{-1}.

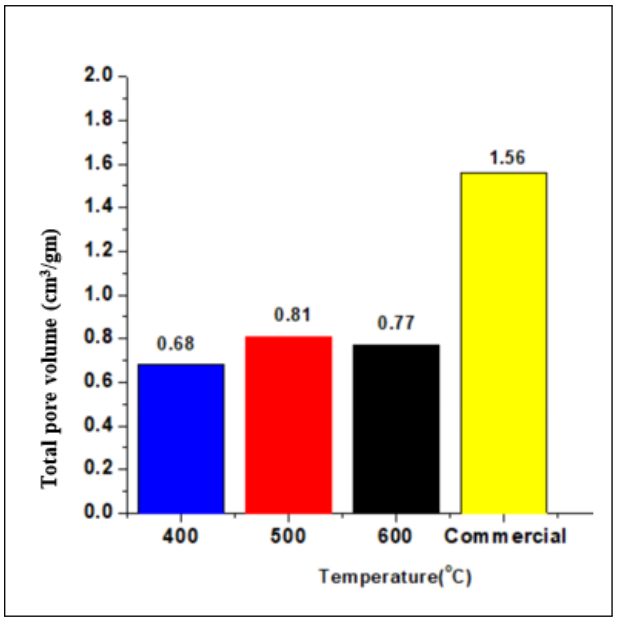

Figure 9: Total pore volume of ACs

3.8 Electrochemical Analysis of AC

The figure alongside shows the CV profile of the activated carbon at different temperatures. This measurement was done on scan rate of 5mV per seconds under the basic electrolyte of KOH and the area of voltammogram was calculated to calculate the specific capacitance.

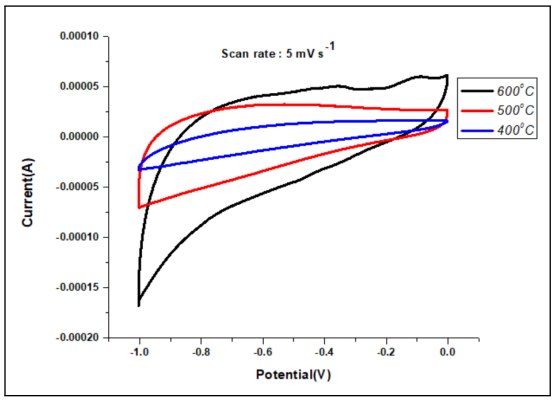

Figure 10: Voltammogram of S_2

The voltammogram of the activated carbon sample prepared at different temperatures are shown below.

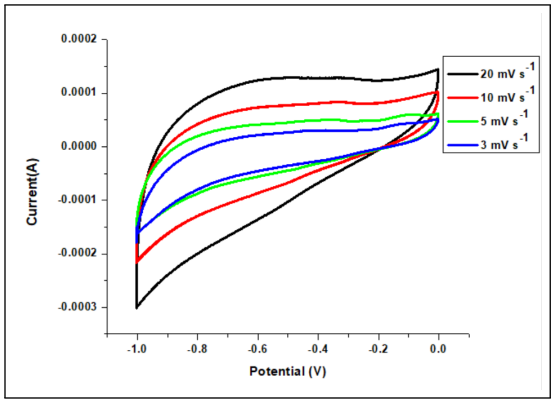

Figure 11: Voltammogram of S_{400}

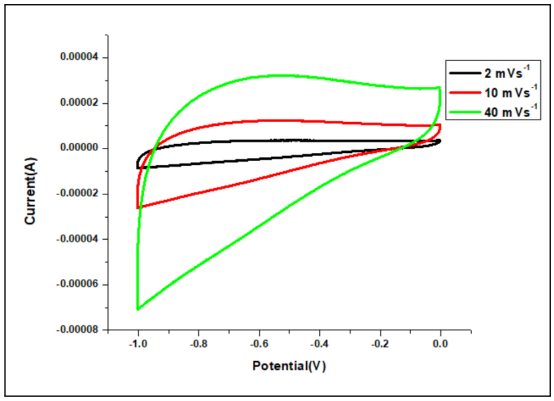

Figure 12: Voltammogram of S_{500}

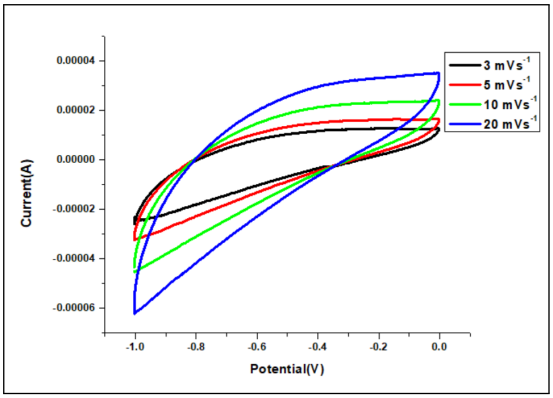

Figure 13: Voltammogram of S_{600}

As the scan rate is increased for the sample of the material, the area of the CV curve in

4. Conclusion

In order to prepare a good electrode for energy storage devices , the specific capacitance of the prepared electrode should be significant. In our research we prepared the electrodes using Activated Carbon and checked it's voltammogram. The cyclic voltammetry graph revealed that the carbon prepared at higher temperature of 600 ^{0} C has higher specific capacitance but the methylene blue number of the AC prepared at 500 ^{0} C is higher. The error bar of the calculated methylene blue number reveals the highest methylene blue number can be any one of the sample prepared at both 500 ^{0} C and 600 ^{0} C as it falls within the error range.Hence, we could synthesise an electrode using a novel and local material.The maximum value of Iodine Number, Methylene Blue Number, were 307 mgg^{-1}, 842.58 mgg^{-1}, for AC prepared at 500^0 C. This was comparable to the commercial carbon with which we have compared all the data.[14] The voltammogram of the sample matched with the voltammogram of AC. This research also reveals a low cost and easy method to synthesize AC from bio waste material.

5. Acknowledgement

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