(ANPA Conference 2023)
ISSN: 2392-473X(Print), 2738-9537 (Online)

Research Article ©Nepal Physical Society
DOI: http://doi.org/10.3126/jnphyssoc.v9i3.62452

Influence of Precursor Type on Activated Carbon Prepared by Phosphoric Acid-Chemical Activation for Supercapacitor Applications

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Abstract.
Phosphoric acid can be used to activate different precursors and produce activated carbon (AC), a porous material with high adsorption capacity and surface area. This research shows how AC is made using different locally available precursors, namely amla seeds and harro seeds. We compare how the carbonization temperature and the precursor type affect the surface area, pore structure, and electrochemical properties of the AC. We use different methods to analyze the AC samples, such as scanning electron microscopy, surface area, methylene blue number, iodine number, and cyclic voltammetry. We show that the best conditions for making AC depend on the type of precursor and the activation temperature.

Received: 31 August, 2023; **Revised**: 17 December, 2023; **Accepted**: 19 December, 2023

Keywords:AC; Energy Storage; Super Capacitor.

1.INTRODUCTION

In the quest for sustainable and efficient energy storage, carbon materials offer a promising solution [1]. But how does the source of carbon affect its properties and performance? This paper examines the role of precursor type on the synthesis and electrochemical behavior of carbon materials produced by phosphoric acid activation, and compares their suitability for supercapacitors.

The growing demand for energy, the scarcity of fossil fuels and the environmental impact of greenhouse gases require renewable energy sources and innovative energy storage solutions [2]. Supercapacitors are a type of energy storage device that have many advantages, such as fast charging and discharging [3], long lifespan [4], high specific capacitance, high power density, environmental friendliness, and resistance to harsh conditions [5], making them suitable for energy systems. AC materials are commonly used as electrodes in supercapacitors [4].

AC is a carbonaceous material that has undergone a treatment process in bio-based precursors to create numerous small pores with low volume [6]. These pores enhance the surface area of the material for adsorption or chemical reactions [7]. Chemical activation is a low-temperature method of producing AC with a large surface area and high porosity by impregnating a carbon source with a chemical agent that removes non-graphitic parts [8]. Different activating agents such as H_3PO_4,H_2SO_4, $ZnCl_2$ can be used for the preparation of AC. Among these phosphoric acid is the most suitable one because it is environmentally friendly,can be easily removed by washing with water and the recovered acid can be reused too [9]. The precursors we selected in this research study are Amla seed (*Phyllanthus emblica*) and Harro seed (*Terminalia chebula*). These are locally available precursors [10].

A previous work demonstrated that zinc chloride AC from amla seeds, barro and harro seeds showed the necessary characterization suitable for an electrode material of a supercapacitor [11, 12, 13]. In contrast, there was no literature in the use of phosporic acid as an activating agent for harro and amla seeds even though the phosphoric acid is environmentally friendly. The seeds of amla and harro fruits available in Nepal [14] are discarded as agricultural waste and had not been studied in this regard. The objective of this study is to compare the AC prepared from the phosphoric acid activation of these locally available precursors in their characteristics and electrochemical properties at the temperature of 400, 500, 600 and 700^{o}C. The ACs from the two precursors are compared using Methylene Blue number(MB_N), Iodine number(I_N),surface area. We also tested the ACs for their electrochemical behavior by using cyclic voltammetry (CV).

2.MATERIALS AND METHODS

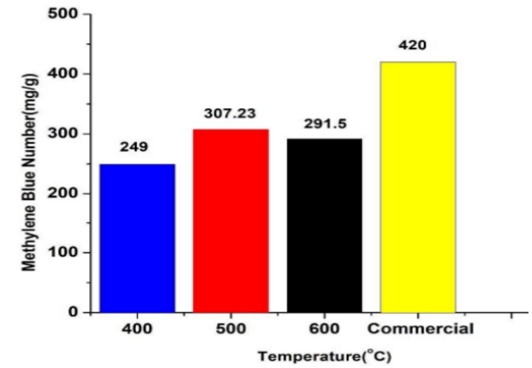
The precursors of the amla seeds and harro seeds were collected from the the local market in Kathmandu.The reason for selecting these particular seeds were that they were widely available as these plants were used for medicinal purposes and their dry old seeds were considered a waste product. Hence, there were environmental and economic benefits to all those involved with these plants. Analytical grade chemicals were used for all the experiments. The nitrogen gas had ultra high purity (UHP) grade. Phosporic Acid (H_3PO_4) was supplied by Merck, Mumbai, India. A methylene blue stock solution was prepared by dissolving 1 g of methylene blue in water and then diluting it to 1000 mL [15]. Standard solutions with different concentrations were obtained by further diluting the stock solution. Distilled water was used for all the experimental purposes [16].

2.1 Preparation of AC

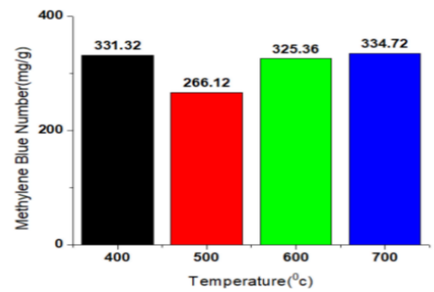
The stones of amla seeds, which were peeled and washed after buying them from the market, were crushed and pulverised. Then, they were mixed with an 1:1 impregnation ratio of Phosphoric Acid; i.e, 33 ml of acid for 15 gm of precursor. The mixtures were heated on a hot plate until they became somewhat dry, and then they were baked in an oven at 100 degrees Celsius for a day. After that, the dried mixes were placed in a quartz tube inside a horizontal tubular furnace and carbonised at different temperatures ranging from 400 to 700 degrees Celsius under a constant flow of nitrogen gas at 100 mL/min for four hours.The carbon samples were filtered and washed with distilled water using a funnel. Then, they were dried in a vacuum oven at 100 degrees Celsius for three hours. The samples were kept in sealed containers for further characterization.

2.2 Characterization of AC

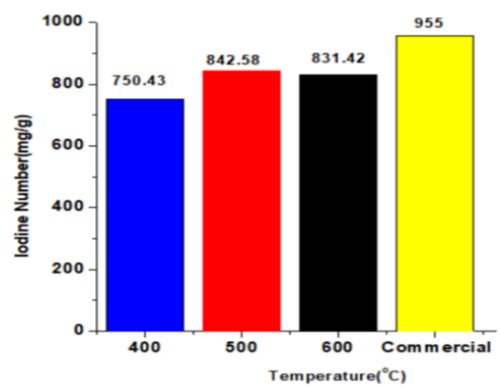
The iodine number of ACs was measured using the ASTM D4607-94 method.The full form of ASTM is



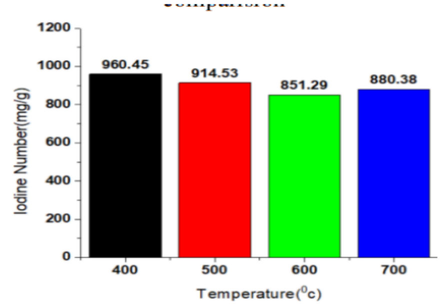
a) Methylene Blue number of AC of Amla seeds for 400 to 600 ^{o}C along with commercial carbon for comparision



b) Methylene Blue number of AC of Harro seeds for 400 to 700 ^{o}C



c) Iodine number of AC of Amla seeds for 400 to



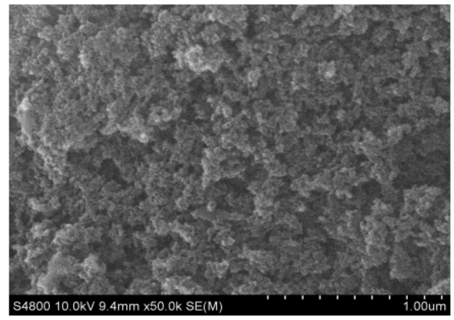
d) Iodine number of AC of Harro seeds for 400 to 700 ^{o}C

Figure 1: Methylene Blue and Iodine number of Harro and Amla AC at different temperatures

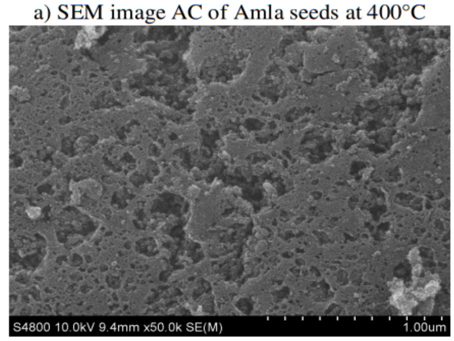
ASTM International, which was formerly known as the American Society for Testing and Materials. An accepted test procedure for determining the AC's iodine number is ASTM D4607-94. The relative degree of carbon activation caused by iodine adsorption from an aqueous solution is measured by the iodine number. The test procedure involves immersing three distinct weights of carbon in a standard iodine solution, filtering the solutions to remove the carbon from iodine, and then titrating the iodine that is still in the filtrate. For every gram of carbon, the amount of iodine adsorbed is computed and used to plot an adsorption isotherm [17]. The methylene blue number of ACs was obtained by using single point adsorption isotherm studies following the standard method [15]. The surface area of ACs was calculated by multiple regressions using the iodine and methylene blue numbers [18]. The ACs were examined by a scanning electron microscope (SEM) from National Institute for Material Sciences in Japan, to study their surface morphology [19]. The CV measurements were taken in Nanolab,Pulchowk campus for studying the electrochemical properties of AC [20].

2.3 Electrochemical analysis of the AC

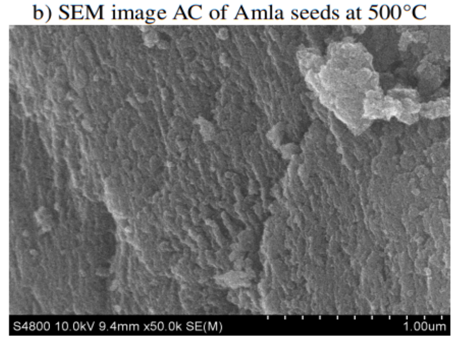
One way to investigate the electrochemical behavior of a substance is to use cyclic voltammetry(CV), which is a technique that applies a varying voltage to an electrode and measures the resulting current. This technique can reveal how a substance undergoes oxidation and reduction reactions in a solution or on the electrode surface. By plotting the current as a function of the voltage, one can obtain a cyclic voltammogram, which shows the characteristic peaks and troughs of the redox reactions. Cyclic voltammograms can provide useful information about the redox potentials, number of electrons involved, reaction rates, and diffusion rates of the substance [21].The voltammogram of the AC at different temperature was taken for the electrochemical study of the AC. The shape of the voltammogram can determine if the AC is suitable for energy storage purpose.



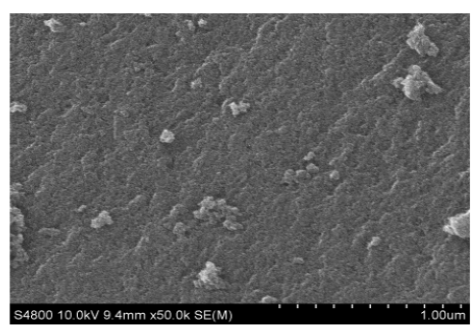
a) SEM image AC of Amla seeds at 400°C



b) SEM image AC of Amla seeds at 500°C



c) SEM image AC of Harro seeds at 400°C



d) SEM image AC of Harro seeds at 500°C

Figure 2: SEM images of AC of Amla and Harro seeds at different temperature

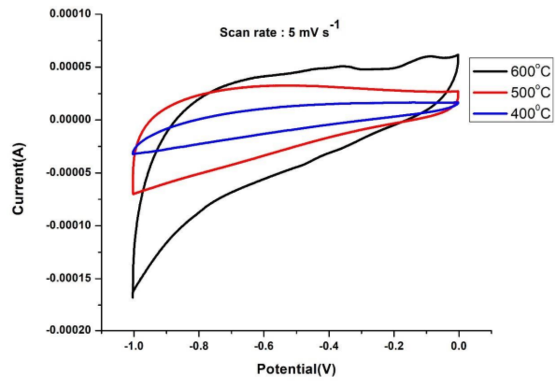
3.RESULTS AND DISCUSSION

3.1 Iodine Number, Methylene Blue Number

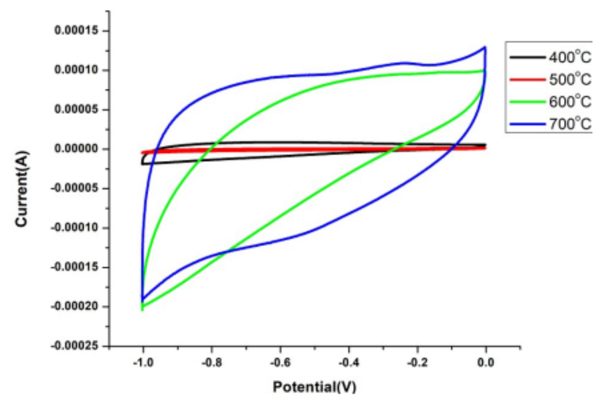
The micropore content of the AC, which are the pores with diameters less than 20 Å, can be estimated by the iodine number (I_N). The I_N is the amount of iodine in milligrams that can be adsorbed by 1.0 g of adsorbent [17]. The iodine number is the most important parameter for characterizing the performance of AC. It is a measurement of activity level; a larger value denotes a higher level of activation. It is commonly given in (mg/g), with a typical range of 500–1200 mg/g. The measurement of AC's micropore content (0–20, or up to 2 nm) is carried out using iodine adsorption from solution. It equates to 900–1100 m^2 /g of carbon surface area [22]. For amla and harro seeds the highest values of iodine number were 831 and 960 mg/g respectively as shown in figure 1 c) and d). This shows amla had the higher micropore content at 400 ^{o}C.

The methylene blue number measures the mesopore content of the AC [15]. The AC's pore size distribution is indicated by the methylene blue number. Larger pores can adsorb more dye molecules, resulting in higher methylene blue numbers. Temperature increase generally increases the pore size and surface area of carbon, which increases its adsorption capacity. The carbon may, however, undergo thermal deterioration at excessive temperatures, which lowers the carbon's adsorption capacity. Thus, the methylene blue value is maximum within a specific temperature range for every variety of AC [23].

The methylene blue number differs for different temperature and precursors as shown in figures 1a) and b). The figure a) indicates that the Methylene Blue Number increases as the temperature rises from 400°C to 500°C, decreases slightly at 600°C, and is highest in the commercial sample. This suggests that the commercial sample has the most significant pore size distribution and that heating the sample can affect the pore size.Figure 2 shows the Methylene Blue number of AC from Harro seeds for different temperatures ranging from 400°C to 700°C. The graph shows that the Methylene Blue number increases slightly as the temperature increases, which means that the pore distribution also increases. This could be due to the activation of the AC by phosphoric acid which can enhance the porosity and surface area of the AC [7]. Figure 1c) shows the Iodine number of AC from Amla seeds for different temperatures ranging from 400°C to 600°C, along with a commercial carbon for comparison.The graph shows that the Iodine number increases as the temperature increases, which means that the micropore content also increases. This could be due to the removal of volatile matter and the development of more pores by the thermal decomposition of the AC [18]. Figure 1d) shows the Iodine number of AC from Harro seeds for different temperatures ranging from 400°C to 700°C. The graph shows a similar trend as Figure 1c), with the Iodine number increasing as the temperature increases. This means that the AC from Harro seeds also has a high micropore content and surface area, especially at higher temperatures.



a) CV of AC from Amla seeds at 5 scan rate.



b) CV of AC of Harro seeds at 10 scan rate.
Figure 3: CV of AC from Harro and Amla seeds at different temperature and scan rate.

3.2 Scanning Electron Micrography

The surface physical morphology of the AC samples was examined by using SEM.The figure shows the scanning electron micrographs of the ACs activated by H_3PO_4 at different temperatures. The SEM images reveal the distinct surface morphology of the ACs depending on the temperature [24]. The chemical activation process increased the pore diameter and pore volume and created new pores as a result of the reaction between the lignocellulosic material and the activating agent [9]. This result was also confirmed by the iodine and methylene blue numbers. It suggested that the temperature and the precursor type had a significant influence on the surface morphology of the different ACs.The electron micrographs of the ACs at different temperatures reveal the microporous character of the AC.

The image at figure 2 a) shows that the surface of the Amla seeds at 400°C appears rough and granular with various sizes of particles clumped together. This indicates that the heating process has altered the physical structure of the seeds and created some pores on the surface. However, the surface is not very smooth or uniform, which suggests that the activation of the AC is not very effective at this temperature. Image b) shows an SEM image of AC from Harro seeds at 500°C, displaying a rough, porous surface texture.Image c) shows an SEM image of AC from Harro seeds at 500°C, revealing a smoother but still textured surface compared to the Amla seeds. The surface texture of the AC suggests a lower surface area and adsorption capacity than the Harro seeds.Image d) shows an SEM image of AC from Harro seeds at 500°C, where the surface appears more porous than at 400°C. This implies that the higher temperature increases the activation of the AC and the development of pores.

3.3 Electrochemical Analysis of AC

The figure 3 shows the voltammogram of the AC at different temperatures. This measurement was done on scan rate of 5mV per seconds under the basic electrolyte of Potassium hydrooxide (KOH). The CV curve had a leaf like shape because the ions moved fast towards the electrodes as the scan rate increased. The graph in a) shows the current (in amperes) versus the potential (in volts) for three different temperatures: 400°C, 500°C, and 600°C. Each curve represents a cycle of increasing and decreasing the potential between -1 V and 0 V. The graph shows that the AC from Amla seeds at 500°C has the highest current response and the largest area under the curve, which means that it has the highest capacitance and charge storage capacity. The AC from Amla seeds at 400°C has the lowest current response and the smallest area under the curve, which means that it has the lowest capacitance and charge storage capacity.The graph also shows that the current response is higher in the negative potential region than in the positive potential region.

The graph in figure b) shows the cyclic voltammetry (CV) of AC derived from Harro seeds at different temperatures (400°C, 500°C, 600°C, and 700°C) at 10 scan rate. The graph shows that the AC from Harro seeds at 700°C has the highest current response and the largest area under the line, which means that it has the highest capacitance and charge storage capacity. The AC from Harro seeds at 400°C has the lowest current response and the smallest area under the line, which means that it has the lowest capacitance and charge storage capacity. The AC from Harro seeds at 500°C and 600°C have moderate current responses and areas under the lines, which means that they have moderate capacitance and charge storage capacities. The shape and area of the curves indicate the capacitive behavior of the AC, which depends on the temperature and the activation process of the Amla seeds. The CV plot did not have any redox peaks, so the Electric Double Layer Capacitor (EDLC) had a capacitive property from the ion accumulation between the electrodes instead of the ions being intercalated/deintercalated [25]. The CV curve showed that the AC could form the double layer on its surface, which means it could be used as an EDLC supercapacitor.

4. CONCLUSION

Phosphoric acid was the activating agent for making the AC, because zinc chloride was bad for the environment and KOH needed high temperature. Phosphoric acid was also easy to get. The temperatures of 400°C, 500°C , 600°C and 700°C were chosen based on the thermogravimetric analysis (TGA) data. The characterization of the samples showed that the AC of amla seeds made at 500 degrees had the biggest surface area, as it also had the highest methylene blue number and iodine number.The AC obtained from harro seeds at 700°C had a perfect rectangular shape in the CV profile. This shows that this AC sample was of high quality and had a high capacity for ion transfer. Therefore, it can be used for energy storage devices.Hence,we can confirm that the effect on the energy storage was mainly due to the choice of the precursor and the temperature at which the precursor was activated.

ACKNOWLEDGMENTS

The authors express their gratitude to the Nanomaterials Lab of the Department of Applied Sciences and Chemical Engineering, Pulchowk Campus, and National Institute for Material Sciences in Japan for their valuable support and help with the research work.

EDITORS' NOTE

This manuscript was submitted to the Association of Nepali Physicists in America (ANPA) Conference 2023 for publication in the special issue of Journal of Nepal Physical Society.

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