PREPARATION AND CHARACTERIZATION OF *Shorea robusta* (SAAL) BARK BASED ACTIVATED CARBON AND STUDY OF ITS ELECTROCHEMICAL PERFORMANCE

A DISSERTATION SUBMITTED FOR THE PARTIAL FULFILMENT OF THE PRE-REQUIREMENTS OF MASTERS OF SCIENCE DEGREE IN CHEMISTRY

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BOARD OF EXAMINER AND CERTIFICATE OF APPROVAL

This dissertation entitled, "**Preparation and characterization of *Shorea robusta* (Saal) bark based activated carbon and study of its electrochemical performance"** by **Mr. Kuldip Joshi** under the supervision of **Assistant Professor Dr. Deval Prasad Bhattarai**, Department of Chemistry, Amrit Campus, Tribhuvan University, Kathmandu, Nepal, and under co-supervision of Asst. Prof. Hari Bhakta Oli, Department of Chemistry, Amrit Campus, Tribhuvan University, Kathmandu, Nepal, hereby submitted has been approved for partial fulfillment of the requirement for completion of the Master of Science (M.Sc.) Degree in Chemistry. This dissertation has not been submitted to any other university or institution previously for the award of a degree.

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LETTER OF RECOMMENDATION

This is to recommend that the dissertation work entitled, "**Preparation Preparationand characterization of *Shorea robusta* (Saal) bark based activated carbon and study of its electrochemical performance** " has been carried out by **Mr. Kuldip Joshi** as partial fulfillment for the requirements of Master of Science Degree in Chemistry. This is his original work and has been carried out under our guidance and supervision. To the best of our knowledge, this research work has not been submitted for any other degree at this institute.

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DECLARATION

I, Kuldip Joshi, hereby declare that the work entitled "**Preparation and characterization of *Shorea robusta* (Saal) bark based activated carbon and study of its electrochemical performance"** submitted to the Department of Chemistry, Amrit Campus, Institute of Science and Technology, Tribhuvan University, Nepal as partial fulfillment for the requirements of the Master of Science Degree in Chemistry have been done by myself and has not been submitted earlier in part or full in this or any other form to any other university/institute, here or elsewhere for the award of any degree.

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Kuldip Joshi

Abstract

In this work, activated carbon (AC) was prepared in the laboratory using *Shorea robusta* (Saal) bark by charring with conc. sulphuric acid followed by phosphoric acid activation with different ratios of precursor to an activating agent at a different temperature on a fixed time. As-prepared activated carbon was characterized by methylene blue number (MBN) and Iodine number (IN) method. The methylene blue number was found to be 193.8802 mg/g whereas iodine number was found to be 2108.2 mg/g. AC-15 at 600 °C for 3 hours had the highest value of methylene blue number which indicated the presence of micropore as well as mesopore in the prepared material. The phase state of the sample was determined by X-ray diffraction (XRD) technique which indicates a predominantly amorphous nature of the prepared material. The surface functionality of the sample was examined by Fourier Transform Infrared Spectroscopy (FTIR) which showed the presence of O-H, aromatic C-C, C-O, and aromatic compounds. Further electrochemical characterization of prepared materials AC-400 and AC-500 were carried out by cyclic voltammetry at a scan rate of 3 mV/s. Specific capacitance of the as-synthesized material was calculated from the measurement of absolute area of cyclic voltammetry curve. The specific capacitance recorded in this work is 76.67 Farad/g. This value shows that AC-500 could be used for electrical double-layer capacitor (EDLC) applications.

Keywords: *Shorea robusta, activated carbon, chemical activation, Cyclic voltammetry, EIS, Specific capacitance*

LIST OF ABBREVIATIONS

DW : Distilled Water
XRD : X-Ray Diffraction
FTIR : Fourier Transform Infrared Spectroscopy
UV : UltraViolet
AC : Activated Carbon
MBN : Methylene Blue Number
IN : Iodine Number
ppm : Part Per Million
RPM : Rotation per Minute
CV : Cyclic voltammetry
EIS : Electrochemical impedance spectroscopy
EDLC : Electrical double-layer capacitor
CGE : Carbon glassy electrode

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CHAPTER 1

1. INTRODUCTION

1.1 General introduction

The term "biomass" refers to all living materials, whether plant or animal. Plant biomass is the most common type of biomass resource. Materials left over from agricultural and forestry activities, as well as organic industrial, human, and animal wastes, etc. are examples of biomass. Such biomas can be employed for the generation of biochar. The baiomass can be converted into biochar by the conventional combustion process (Tan et al., 2017).

Charcoal is a light black carbon residue made by burning wood (or other animal and plant sources) in a low-oxygen environment by eliminating all water and volatile components. Charcoal is an odorless, fine black powder or black porous solid made up of carbon and any remaining ash that is obtained by eliminating water and other volatile elements from animal and plant matter. Charcoal is produced by the incomplete combustion of plant or animal products. Charcoal has been used for a variety of reasons from the beginning of time, including in medicine and art, but its most prominent application has been as a metallurgical, cooking, industrial, and automobile fuel (Abdollahi & Hosseini, 2014).

Activated charcoal, also known as activated carbon, is a fine black powder prepared formed from animal or plant-based materials such as charred bones, coal, petroleum coke, and coconut shells, and so on. Traditional activated carbon feedstocks include wood, coal, petroleum wastes, peat, lignite, and polymers, all of which are expensive and non-renewable sources. As a result, several researchers have focused on producing activated carbon from low-cost and sustainable alternative precursors such as agricultural residues (rice husk, corn straw, bagasse, and so on) and solid wastes (sludge, food waste, garden waste, etc.). The availability of low-cost precursors is required for the economic feasibility of large-scale activated carbon manufacturing, hence producing activated carbon from waste and by-products has received interest (Tan et al., 2017).

AC has been manufactured from biomass materials using a physical or chemical activation procedure in recent decades and is now widely employed in various industrial applications because of their remarkable porosity architectures for ion adsorption-desorption without any chemical interactions. In general, biomass is carbonized and subsequently activated at high temperatures in an inert atmosphere or steam to produce AC through physical activation. During chemical activation, biomass is impregnated with an activating agent (such as acids, bases, or Saalts) and then carbonized at temperatures ranging from 450 to 900 degrees Celsius (Awasthi et al., 2019).

The majority of organic substances with high carbon content could be used as AC raw materials. The aspects listed below can be considered when creating a porous carbon structure.

i. There is a lot of carbon in nature.
ii. Low inorganic content (low ash)
iii. The potential extent of activation
iv. Low storage degradation
v. High density and sufficient volatile content
vi. Supply stability in the countries
vii. Inexpensive materials

Lignocellulosic materials are commonly employed as a precursor for the production of AC and account for roughly 45 percent of the total raw materials required. It is critical to get materials with a low inorganic content to manufacture AC with low ash content. A somewhat high volatile content is required for full control of the production process (Tadda et al., 2016).

It has been reported that the activated carbon can be synthesized from various biomass materials i.e lotus seed (R. L. Shrestha, R. Chaudhary, et al., 2020), jack fruit seed (Chaudhary et al., 2020), *Wisteria sinesis* seeds (Awasthi et al., 2019), lapsee seed (L. K. Shrestha et al., 2020), washnut seed (R. L. Shrestha, T. Shrestha, et al., 2020), Corncub (Adhikari et al., 2015),cotton (Liu et al., 2016), etc.

All-natural biomasses and agricultural wastes are lignocellulosic materials, and comprise cellulose, hemicellulose, and lignin, which can be exploited to generate biochar with a low specific surface area and low porosity upon pyrolysis in the temperature rang of 200-300 °C. The chemical or physical activation of these biochars results in the creation of a porous structure with a large surface area (Chaudhary et al., 2020). By using a physical activation technique, biomass can be carbonized and then activated at high temperatures in an inert atmosphere to produce activated carbon. During chemical activation, biomass is impregnated with activating chemicals followed by carbonization at temperatures ranging from 450 to 900 °C (Chaudhary et al., 2020). Activating agents often employed during the activation process include dehydrating Saalts such as zinc chloride $ZnCl_2$, sodium carbonate Na_2CO_3, phosphoric acid (H_3PO_4), and alkali (NaOH, KOH). To increase the specific surface area, it's critical to choose the proper activating agents and carbonization parameters because of its outstanding properties such as high surface area, abundance in nature, low cost, higher endurance, reduced corrosivity, and a wide operating temperature, activated carbon is widely utilized as a various industrial application (Karnan et al., 2016). Surface area, pore structure (size, volume, and shape), and resistive/conductive behavior materials determine the utility of activated carbons for electrochemical aplications. Because of their tunable surface properties and lower cost in comparison to other carbon materials, activated carbons can serve as porous carbon materials for their applications in various sectors such as batteries, supercapacitors, fuel cells, metal ions adsorption and so on (Gurten Inal & Aktas, 2020).

1.2 Activated carbon

Activated carbon, also known as activated charcoal or activated coal, is a type of carbon that has been processed to have small, low-volume pores, making it extremely porous and allowing it to have a huge surface area ($>1000\ m^2g^{-1}$) available for adsorption or chemical reactions (Tadda et al., 2016). Activated carbon is a substance with a large specific surface area, outstanding porosity, high physiochemical stability, and great surface reactivity which can be commonly used as a functional material in a variety of applications. Activated carbon is a primarily amorphous material with an enormous internal surface area and pore volume. Activated carbon is a good adsorbent because of these unique features and it is frequently employed in industrial applications (Baker et al., 2000). AC can be made by treating carbonaceous materials with oxidizing gases (such as steam, air, or carbon dioxide) or dehydrating chemicals (such as H_3PO_4, H_2SO_4, $ZnCl_2$, or KOH) (Olivares-Marín et al., 2009).

1.3 Preparation of activated carbon

The biomass is transformed into porous carbon using a combination process of carbonization and chemical activation for the synthesis of biomass-derived carbon material. During carbonization, heteroatoms in the waste material's backbone are removed, resulting in the production of carbon skeletons and the formation of porous structures(Jain, Ghosh, Krajewski, Kurungot, & Michalska, 2021). In general, physical and chemical activation are the two most frequent methods for producing activated carbon. However, simple thermal activation in a nitrogen atmosphere and microwave radiation are viable ways of obtaining activated carbon. However, multimodal activation (chemical and physical) should be used to increase textural features and establish hierarchical porosity (González-García, 2018).

1.3.1 Physical activation

A series of steps are involved in the physical activation of carbonaceous materials Carbonization and activation are the two most crucial phases in these processes. Carbonization of biomass (pyrolysis) and carbonization of biochar (full carbonization) is commonly carried out in an inert gas atmosphere at temperatures ranging from 600 to 900 °C. Raw biochar is frequently produced in flue gas or oxygen-limited gas in commercial and laboratory settings. Carbonization eliminates non-carbon species, resulting in biochar with high carbon content. The basic goal of activating raw biochar is to increase the internal surface area by partially gasifying the carbon skeleton. Thermal treatment in a partly oxidizing media (e.g. steam, CO_2, ozone, and restricted air) or an inert agent (He or N_2) is commonly used to achieve this goal (Sajjadi et al., 2019). In most cases, the carbon compounds are activated using a traditional heating procedure. Microwave heating, one of the most recent advancements in heating technology, is a novel approach that has piqued the interest of many academics. Microwave activation is still used at the laboratory scale for the preparation of high porosity carbon products today. Microwave heating has a lot of potential to become a viable alternative to traditional heating technologies in industrial production because of its many benefits. High yield of products, high heating rate, energy transfer instead of heat transfer, selective heating, greater control of the heating process, lower activation temperature, smaller equipment size, and less automation are all advantages of microwave heating over traditional heating methods (Lee et al., 2014).

1.3.2 Chemical activation

Dehydration and pyrolysis are two stages in the chemical processing of the biomass precursor to produce activated carbon. In this process, phosphoric acid, zinc chloride, potassium hydroxide, ammonium chloride, hydrochloric acid, sodium hydroxide, and other chemical reagents are impregnated into raw lignocellulosic precursor (Williams, Reed, & Bioenergy, 2006). The choice of activating reagent, mass ratio of activating reagent to precursor, and operating temperature periods are all closely controlled throughout this process. Dehydrating agents are used to prevent the production of tar and other unwanted products. The precursor-agent mixture is thermally treated at temperatures ranging from 400 to 1000 °C in a controlled environment, and then washed to remove the activating agent. During pyrolysis, a gaseous stream such as air, nitrogen, or argon is typically employed, which improves the material's interior porosity. When the activating ingredient is very alkaline, the chemical agent aids in the development of porosity. The ratio of a chemical agent to precursor determines the pore size distribution and surface area (González-García, 2018). Activators play a critical role in chemical reactions. Phosphoric acid is generally employed as an activator to promote bond cleavage and porosity development (Feng, Li, Wang, & Xu, 2020). Phosphoric acid has a lower activation temperature, and a larger carbon yield, and produces primarily mesoporous structures when compared to other regularly used activating reagents (Han, Wang et al., 2020). $ZnCl_2$ activation results in homogeneous micropores, and pore size increases as $ZnCl_2$ concentration rises (Marsh & Reinoso, 2006). Alkali agents create narrow and wide microporosity, and it has been discovered that the alkali/precursor ratio is a crucial determinant in a raw material breakdown. At low alkali ratios, activation can proceed without disintegration (González-García et al., 2013). Chemical activation of AC has several advantages over physical activation, including one-stage heating, higher yield, and very microporous end products. It is better suited to materials with a higher ash percentage. Aside from these benefits, chemical activation can help achieve desired results by lowering activation temperature, shortening activation time, and improving the development of inner porosity. Chemical activation, on the other hand, has several drawbacks. The technique uses chemicals and corrosive agents which are costly as well as needs subsequent washing and material purification. Besides these, handling of chemicals can be a hazardous and risky activity. As a result, extra precautions are required to reduce the risk to one's health and safety (Lee et al., 2014).

1.3.3 Mechanism of activation

Biomass primarily constitutes cellulose, hemicellulose and lignin. Charring of the biomass results into the dehydration of these hydrocarbon resulting into the production of black char product. However, charring and formation of activated carbon is a temperature dependent function. Primary charcoal is a polymer made up of cellulose fragments that is extremely complicated.

$C_n(H_2O)_n$ + conc. $H_2SO_4 \rightarrow$ n C + $H_2SO_4.nH_2O$

Heat and activating chemicals attack these massive molecules at their most unsaturated sites, removing some carbon and most of the hydrogen from the primary charcoal. The end product is a massive molecular group of carbon atoms held together more or less loosely and blasted through with atomic-sized holes. During activation, the interior surface of charcoal is greatly enlarged, and this alone accounts for the activity created. The first step of wood carbonization creates the appropriate surface and capillary structure to account for the whole amount of adsorption in activated charcoal. Simultaneously, certain oily hydrocarbons are produced and tenaciously adsorbed on the active carbon framework. Activation is the only technique that can burn away the adsorbed hydrocarbons without also burning the active carbon base. The process of activation is the formation of a highly porous substance. The process of activation involves increasing the unsaturation of the charcoal material (Barker, 1930).

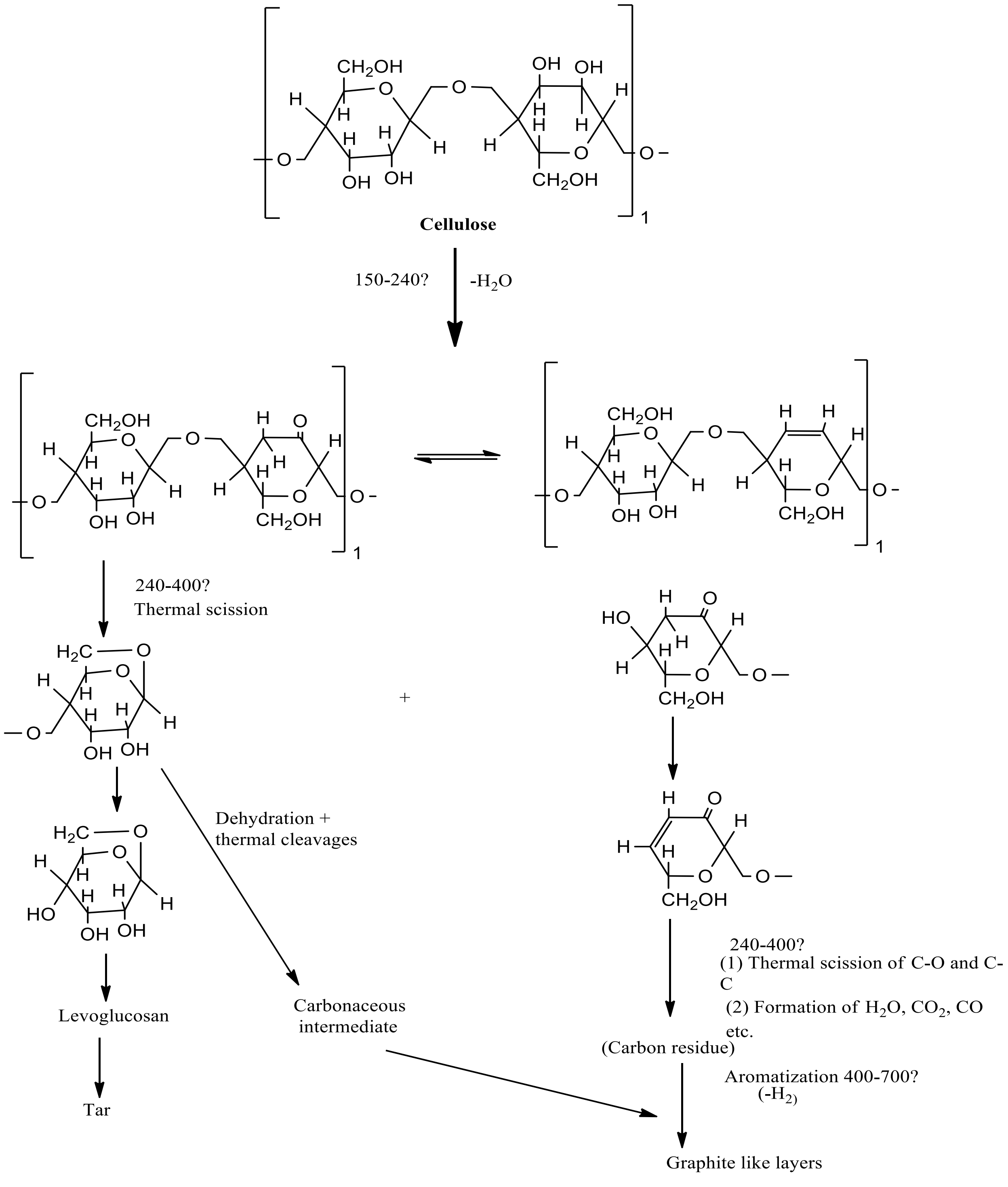

Figure 1: *Mechanistic steps for converting cellulose to carbon*

1.4 Application of activated carbon

Activated carbon is a very effective adsorbent that is widely used in water purification to remove pollutants and unwanted compounds. Powdered activated carbons are those types of compounds that can be used to eliminate the organic compound as well as heavy metal ions from water. Activated carbon is a critical tool used throughout municipal and industrial water treatment facilities to treat drinking water, wastewater, and municipal water for process use (Najm et al., 1991)

Activated carbon is also employed for dye removal, supercapacitor, batteries, oxygen reduction, fuel cell, etc. Presence of a large number of functional groups such as hydroxyl, carboxyl acid groups, etc. can enhance the hydrophilicity of the material whch could be wuseful in the water treatment process (Silva et al., 2017).

1.5 *Shorea robusta* plant.

Scientific classification of *Shorea robusta*

Kingdom:	Plantae
Subkingdom	Viridiplantae
Infrakingdom	Streptophyta
Superdivision	Embryophyta
Division	Tracheophyta
Subdivision	Spermatophytina
Class	Magnoliopsida
Superorder	Rosane
Order	Malvales
Family	Dipterocarpaceae
Genus	*Shorea*
Species	*robusta*
Common name	Saal(साल)

Figure 2: *Shorea robusta plant*

Shorea Robusta, or Saal in Nepali, is a perennial tree of Dipterocarpaceae family (Silva et al., 2017). It is predominantly found in Nepal's Tarai region, especially in the Churai range and several highland subtropical climate zones. *Shorea robusta* forests occupy a total area of more than 10 million hectares in India, Nepal, and Bhutan. *Shorea robusta* trees abound in Nepal's southern lowlands, the Bhabar-Terai, encompassing around 1.4 million hectares. In these forests, the average standing volume is 144 m^3ha^{-1}. Natural *Shorea robusta* forests in Nepal's Bhabar-Terai region feature a clustered, heterogeneous structure (Rautiainen, 1999).

Shorea robusta is a large deciduous tree that can grow up to 50 meters tall and have a diameter of 5 meters; these are exceptional sizes, as most *S. robusta* trees reach a height of 18-32 meters and a diameter of 1.5-2 meters under normal conditions.

Shorea robusta (Saal) is a plant that has long been used in traditional medicine to treat a variety of diseases, including circulatory, digestive, endocrine, pulmonary, and skeletal problems, as well as infectious diseases. Different parts of *S. robusta* contains a different type of organic compounds. Whole plants contain ursolic acid, α-amyrenone, α-amyrin & β-amyrin, the bark contains ursonic acid, oleanane, and Shoreaphenol, the seed contain hopeaphenol and the leaves contain Friedelin β-sitosterol and Dihydroxyisoflavone (Soni et al., 2013). The bark of *S. robusta* is rich in ursolic acid, oleanane, and shoreaphenol. Through exchange or complexation, these functional groups can absorb ions, metals, or substances. These phenomena occur on the surface of a material when ions, metals, or substances interact with the surface's functional group. Infrared spectroscopy is a valuable tool in the quantitative analysis of organic molecules. It is commonly used in the fields of natural products, organic synthesis, and transformations to determine the functional groups present in a sample.

It consists of thick bark about 8-12 mm that is used for treating diarrhea, dysentery, and vaginal discharges. Many secondary metabolites belonging to terpenoids, flavonoids, polysaccharides, lignins, phenols, and sterols have been discovered in phytochemical research. *Shorea robusta* crude extracts and isolated chemicals have a wide range of pharmacological properties, including anti-inflammatory, anti-obesity, antibacterial, wound healing, antipyretic, and analgesic effects (Soni et al., 2013).

Saal is mostly utilized as a building material for furniture and other home items. Aside from it, various sections of saal are utilized for woods, fragrances, coal, and so on. Sawdust and splinters of wood, for example, have a high carbon content in the lignocellulosic form and have a typical chemical composition with low inorganic material and high volatile material (D. Shrestha et al., 2019). Sawdust wastes from carpentry activity is a major source of waste byproducts in addition to the bark of *S. robusta*. These waste by-products have a high carbon concentration in lignocellulosic form, with low inorganic material content and high volatile matter content. Thus, waste *S.robusta* bark can be converted into activated carbon, which is then employed in the various application (D. Shrestha & Rajbhandari, 2021).

CHAPTER 2

2. LITERATURE REVIEW

It has been reported that activated carbon can be synthesized from various parts of biomass such as seed, leaf, stem, waste peel, stone, etc. Nanoporous carbon materials with high surface area have been derived from Lapsi seed agro-waste and activated with zinc chloride ($ZnCl_2$) at 700 ℃. Materials with excellent surface areas and pore volumes have been reported. These Lapsi seed-derived nanoporous carbon materials have high surface areas, large pore volumes, and interconnected mesopore architectures that exhibited good electrochemical performance (L. K. Shrestha et al., 2020)**.**

Activated carbons were prepared from waste sawdust powder from a sawmill. Na_2CO_3 was used to make activated carbon, followed by the carbonization procedure. Iodine Number (IN) and Methylene Blue Number (MBN) were used to analyze the activated carbon. The iodine number was 534.6 mg/g, while the MBN was 196.08 mg/g, indicating the existence of micropores and mesopores in the produced material. The phase condition of the samples was then examined using X-ray diffraction (XRD), which revealed that the synthesized material was amorphous. Fourier Transform Infrared Spectroscopy (FTIR) revealed the presence of oxygenated functional groups. Conductivity testing and cyclic voltammetry were also used to characterize the electrochemical properties of the produced material. The electrical double layer capacitive behavior was shown by the cyclic voltammetric curve, which had a symmetric rectangular form (Shrestha et al., 2018).

Rajbhandari et al. reported the preparation of ACs from sawdust, and three distinct activating agents were used to activate them. H_3PO_4, KOH, and Na_2CO_3 were doped as Sr–H_3PO_4, Sr–KOH, and Sr–Na_2CO_3. TGA/DSC, XRD, Raman, SEM, FTIR, and BET were used to characterize the ACs. The amorphous character of all the ACs as prepared was discovered. At the surface, the oxygen surface functionality was formed. Sr–H_3PO_4, Sr–KOH, and Sr–Na_2CO_3 had excellent surface areas. The total electrochemical performance of Sr-H_3PO_4 demonstrated remarkable supercapacitive performances, indicating that this material has a significant potential for usage in EDLC applications in supercapacitive energy storage (Shrestha & Rajbhandari 2021).

Biomass-derived hard carbon is synthesized from an easy technique, to investigate the viability of employing it in electrochemical supercapacitors. As an electrode for electrochemical energy storage, a low-cost, environmentally benign, and easily manufactured carbon material is used. Four distinct hard carbons were synthesized and evaluated as supercapacitor electrodes from KOH-activated banana stem (KHC), phosphoric acid treated banana stem-derived carbons (PHC), corn-cob derived hard carbon (CHC), and potato starch-derived hard carbons (SHC). According to the cyclic voltammograms, KOH-activated hard carbon has a specific capacitance of 479.23 F/g and exhibits excellent electrochemical performance (Ghosh et al., 2019).

In the work of Shrestha et al., activated carbons were prepared from the *Shorea robusta* and coated with MnO_2. TGA/DSC, SEM, X-ray diffraction (XRD), Raman spectra, Fourier Transform Infrared Spectroscopy (FTIR), Brunauer–Emmett–Teller (BET), and X-ray Photoelectron Spectroscopy were used to analyze the activated carbon. The produced material was found to be amorphous with oxygenated surface functional groups. The cyclic voltammetry curve of activated carbon was found to be nearly rectangular which is the characteristic of electrical double-layer capacitors (EDLCS) (Shrestha et al. 2019).

In the study of Thambidurai, the researcher studied the behavior and performance of sugarcane baggase and rice straw as supercapacitor electrodes. The formation of crystallites of carbon and silica during activation at higher temperatures was revealed by X-ray diffraction. SEM was used to determine the morphology of the carbon samples. Carbon composites' surface area, pore volume, and pore size distribution were all measured. The electrochemical responses were investigated using a three-electrode system in cyclic voltammetry experiment at 25°C. At scan rates of 2-3 mV/s, the specific capacitance of the sugarcane bagasse carbon electrodes was found to be 92-340 F/g, whereas rice straw had a specific capacitance of 56-112 F/g. Using H_2SO_4 as the electrolyte, sugarcane bagasse carbon performed better than rice straw carbon (Thambidurai et al., 2014).

Chemical activation of lignin with $ZnCl_2$, H_3PO_4, and several alkali metal compounds produced activated carbons. Carbonization and activating reagent affects on the pore structure and surface area of activated carbon. In both $ZnCl_2$ and H_3PO_4 activation, the greatest surface areas were attained at a carbonization temperature of 600 ℃, and the surface areas were found comparable to those with commercial activated carbons (Hayashi et al., 2002).

In the work of Sim et al., the authors have reported the physical and electrochemical properties of carbon generated from processed food waste as an electrode material. The eco-green carbon was created through chemical activation with phosphoric acid as the activating agent and activation temperatures ranging from 500 °C to 600 °C and 700 °C. The highest specific surface area was attained, and the material is primarily mesoporous. Using cyclic voltammetry and KOH as the electrolyte, the electrochemical characteristics of activated carbon electrodes were investigated. The specific capacitance determined by cyclic voltammetry was 85 Fg^{-1}. The results showed that carbon derived from processed food waste was a promising electrode material for supercapacitors (Sim et al., 2015).

Because of the well-defined pore architectures, nanoporous carbon compounds derived from biomass have a large surface area. The activation of the *Areca catechu* nut powder with phosphoric acid (H_3PO_4) was used in the preparation technique. On the textural qualities and surface functional groups, the impacts of carbonization circumstances (mixing ratio with H_3PO_4, carbonization time, and carbonization temperature) were investigated. At a 1:1 mixing ratio and 400 °C carbonizations for 3 hours, the sample achieved a high specific surface area and a large pore volume. Amorphous carbon structures and oxygenated surface functional groups characterize the produced materials. The ideal sample demonstrated good iodine and methylene blue adsorption due to well-defined micro and mesopore structures with high surface area and large pore volume. The results for iodine number and methylene blue were approximately 888 mg g^{-1} and 369 mg g^{-1}, respectively (Joshi et al., 2022).

In the work of Joshi et al., activated carbons (ACs) were made from a variety of agricultural wastes, including lapsi seed stones, beleric seeds, peach stones, walnut shells, bamboo, and sugarcane bagasse via pyrolysis process with chemical activation using phosphoric acid. Iodine number, methylene blue number, surface area, scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray diffraction were used to analyze the ACs as they were produced. The AC produced from peach stones yielded the maximum carbon output. The ACs made from peach stones and walnut shells had the largest surface areas. An exterior surface covered with regular holes of various shapes and sizes, an amorphous nature, and identical oxygen-containing surface functional groups may be found on all ACs (Joshi et al., 2021).

As an affordable and effective adsorbent, activated carbon is widely employed in a variety of procedures. The adsorption properties of activated carbon vary depending on the feed materials and activation method used. Agricultural wastes such as bagasse, hard apricot stone shells, almond, walnut, and hazelnut shells were chemically activated with phosphoric acid to make activated carbon. The impact of various preparation variables on the yield and quality of produced carbon was investigated. The findings revealed that the ultimate activation temperature, heating rate, activation time, and chemical agent impregnation rate were all crucial in determining the quality of activated carbon produced. According to the findings, activated carbon derived from apricot stone-hard shells has the best adsorption properties and the largest surface area (Soleimani & Kaghazchi, 2007).

Adhikari et al. prepared nanoporous activated carbons (AC) from low-cost agro-waste corncob powder and activated them with phosphoric acid which results in high surface areas and pore volumes that exhibited excellent electrochemical performance (Adhikari et al., 2015).

2.1 Statement of problems

A large amount of activated carbons are being used in the industry and energy sectors. Activated carbon for such applications is required to exhibit good performance without causing serious effects on the environment and should be available at a low cost. Raw materials required for large-scale production of activated carbon for a commercial application are an utmost issue, these days. The commercial activated carbons are synthesized from the combustion of fossil fuel-based precursors such as coal, gasoline pitch, etc. But these are not environmentally friendly and have limited sources causing less economic benefit. In this context, biomass-based activated carbon can be developed as an alternative source. Biomass-based activated carbon materials have been used for various applications such as energy storage, adsorption, dye removal, etc. because of their outstanding characteristics such as high electronic conductivity, high surface area, low-cost affordability to large-scale applications, and easy synthesis method. Hitherto, different parts of the plant such as Saal saw dust, heartwood, leaf, etc. have been used for the synthesis of activated carbons. To the best of our knowledge, the execution of the bark of the Saal has not been reported for preparation of activated carbon characterized with electrochemical performance.

2.2 Objective of the study

The research mainly focused on the following general and specific objectives.

2.2.1 General objective

Synthesis of activated carbon from *S. robusta* bark and study its electrochemical performance.

2.2.2 Specific objectives

- Preparation of carbonaceous material from *S. robusta* bark by charring with conc. H_2SO_4
- Chemical activation of as-synthesized carbonaceous materials.
- Caracterization of as-synthesized activated carbon.
- Study of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of AC

CHAPTER 3

MATERIALS AND METHODS

3.1 Apparatus used

Common laboratory equipments such as beaker, burette, pipette, conical flasks were used to carry out the experiment. pH meter was used to measure the pH of solution. Double beam spectrophotometer (Company: Labtronics) was used for the measurement of concentration os solution. FTIR spectra were determined using Perkin Elmer spectrometer 10.6.2 version, located in Amrit Campus Thamel Kathmandu Nepal. Shimadzu X-ray diffractometer with monochromatic Cu anode and X-ray tube curved graphite filter monochromator (D2 phase Diffractometer, Burker, Germany) at Nepal Academy of Science and Technology (NAST), Khumaltar, Lalitpur was used for X-ray crystallography. CorrTest Electrochemical Workstation (Wuhan Corrotest Instrument Corp., Ltd, China) was used for the measurement of cyclic voltammetry and Electrochemical Impedance EIS).

3.2 Chemicals used

Chemical test for the work was carried out in wet laboratory. For this research work, distilled water was used where required. Also, for rinsing the sample during analysis distilled water was used. Hydrochloric acid (Qualigens, purity 36%), Nitric acid (Qualigens), Sulphuric acid (Qualigens), and Phosphoric Acid (Qualigens) Methylene blue solution (Mol. mass: 373.90, percentage purity: 98.5%, company: nacalaitesque), sodium thiosulphate (molecular mass: 248.18, company: Qualigens), potassium dichromate (company: Fischer scientific, molecular mass: 294.18), iodine crystal (company: Sara Bhai Merck, molecular mass: 254), starch, Whatman-42 of analytical grade were used. Solutions to these chemicals were prepared following the standard protocols. All the chemicals were used as received without further refinement.

3.3 Collection of sample and preparation of fine powder

The bark of *S. robusta* was collected from the Nareshwar, Gorkha district (Latitude: **28.02,** Longitude: **84.61)**. The bark of *S. robusta* was washed with tap water and chopped into small pieces. These small pieces were washed with tap water and finally distilled water (the conductance of distilled water was 8.5 μSiemen/cm). Then it was dried over sunlight for a week. The sample was again dried in a hot air oven (at 80 °C for 8 h) and the dried bark was grinded with an electric grinder to obtain fine powder and sieved to 250-micron particle size using sieving mesh.

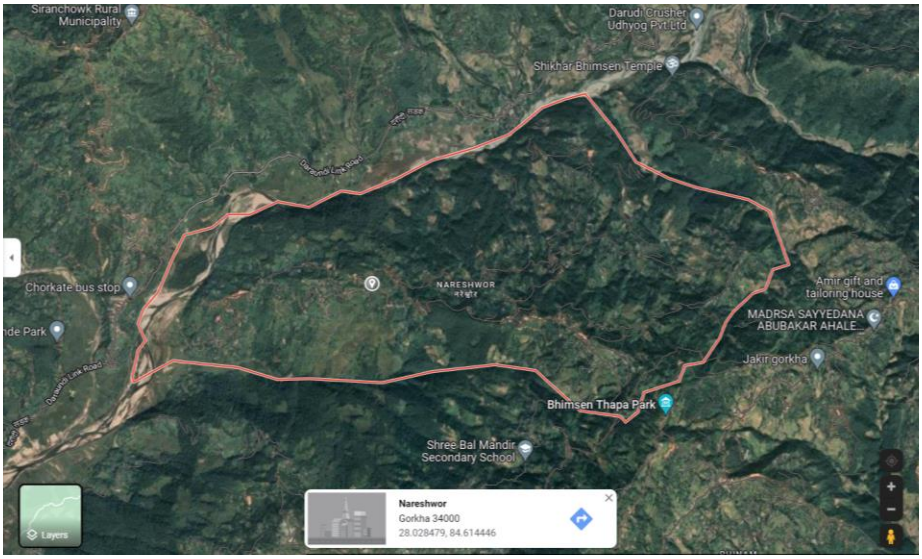

Figure 3: *Google map of the sample collection area*

3.4 Preparation of *S. robusta* char

235.4 g of fine powder of *S. robusta* was charred by concentrated sulphuric acid. Acid was added slowly into the fine power of *S. robusta* in installment in a fume cupboard and stirred with a glass rod until the brown color of *S. robusta* turned into a black color. Black char was left for 24 hours at room temperature and washed with tap water (conductance of tap water 5.63×10^{-4} Mho cm^{-1}). Washing was repeated several times until it attains near about neutral pH value (pH 5.92). Finally, the black char was washed with distilled water and dried in a hot air oven at a temperature of about 100 ℃ for 9 hours. Finally, we get powdered biochar. The weight of biochar was 122.4 g. The char was pre-carbonized at temperature (290 ± 10 ℃) for 4 hours in the muffle furnace as per the protocol of Shrestha et al. (Shrestha et al. 2019).

The methodology process is shown in the given chart below.

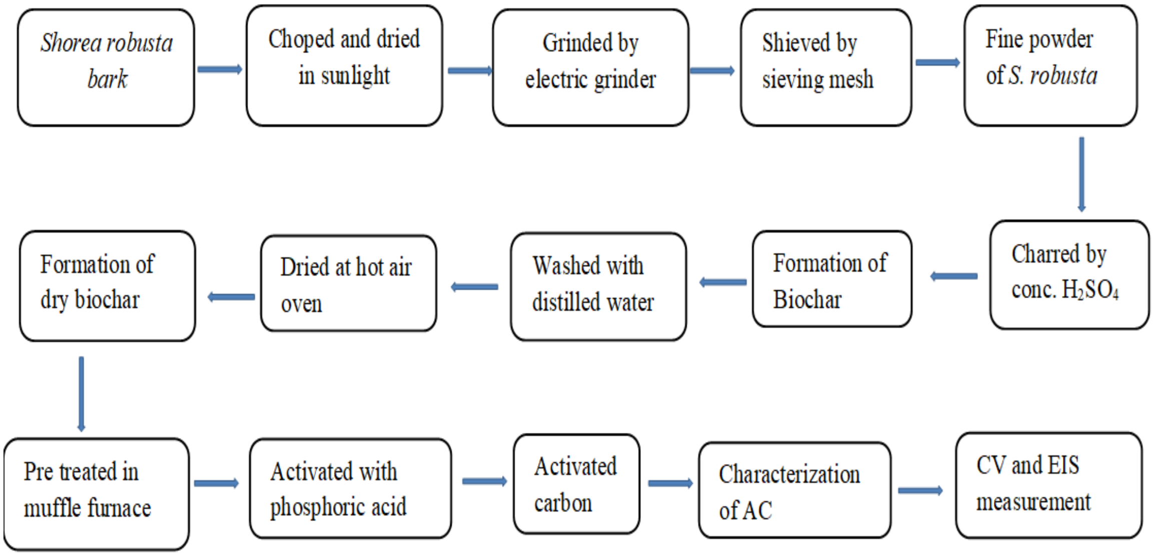

Figure 4:*Methodology process*

3.5 Activation of Precursor

To find the optimum condition for the preparation of nanoporous activated carbon from the pre-activated powdered precursor, a series of activated carbon using 65% orthophosphoric acid as an activating agent was prepared. For this, the pre-carbonized powdered precursor was activated with 65 % orthophosphoric acid at different ratios and temperatures for 3-hour duration in the muffle furnace. The carbonized activated carbon was cooled at room temperature and washed with distilled water until the pH was neutral. Finally, it was completely dried in a hot air oven at 110 ℃ and kept in an airtight viles tube for further research (Hayashi et al., 2000).

3.6 Effect of doses of activating agent

A list of different samples made by mixing powder carbon (PC) and activating reagent (AR) in their mass ratio is presented in table number 1. Sample with PC and AR in 1:3 ratio is named as AC-13 and so on for other sample. Each sample was activated at 300 ℃ for 3 hours.

Table 1: *Variation of dose of activating agent*

Activated carbon	Ratio of powdered precursor and phosphoric acid	Carbonization temperature(°C)	Carbonization time (h)
AC-13	1:3	300	3
AC-14	1:4	300	3
AC-15	1:5	300	3
AC-17	1:7	300	3

The four samples were used to determine the MB number and Iodine number. The sample of optimized ratio was processed for the optimization of temperature.

3.7 Effect of Carbonization temperature

The AC-15 was taken as optimized sample and the effect of temperature was studied under three different temperature which is presented in the table 2. The sample with powder carbon and activating reagent in 1:5 heated at 300 °C is named as AC-300 and so on for other samples.

Table 2: Variation of carbonization temperature

The ratio of powdered precursor and phosphoric acid	Activated Carbon	Carbonization temperature(°C)	Carbonization time(h)
AC-15	AC-300	300	3
	AC-400	400	3
	AC-500	500	3
	AC-600	600	3

3.8 Reagent preparation

Different solutions and reagent required for various tests are prepared as follows.

1000 ppm methylene blue stock solution

0.2922 g of hydrated methylene blue solution was dissolved in distilled water in a 250 mL-volumetric flask and diluted up to the mark. Then the stock solution was diluted to 100 ppm and 10 ppm. Finally, 1 to 9 ppm of methylene blue solution was prepared by serial dilution method.

Preparation of 500 mL of 5% HCl solution

69.44 mL of HCl was added to about 400 mL of distilled water in a 500 mL volumetric flask in installment wise in a fume cupboard with frequent shaking of the solution. Finally, the solution was made up to the mark.

Preparation of 500 mL of 0.1 N Sodium thiosulphate solution

12.41g of sodium thiosulphate was dissolved in approximately 75 mL of freshly boiled and cooled distilled water. 0.05g of sodium carbonate was added to minimize bacterial decomposition of the thiosulphate solution and transferred the mixture to a 500 mL volumetric flask and diluted up to the mark.

Preparation of 100 mL of 0.1 N $K_2Cr_2O_7$ solution

0.4903 g of potassium dichromate was dissolved in a 100 mL volumetric flask and diluted up to the mark with distilled water.

Preparation of 500 mL of 0.1 N iodine solution

6.35 g of iodine crystal and 9.55 g of potassium iodide were mixed in a beaker. 5mL of distilled water was added to the beaker and stirred well. Further added 5mL DW each time with constant stirring and made the volume to 50 mL. The solution was allowed to stand for 4 hours to ensure complete dissolution of iodine crystal. The solution was transferred in v.f of 500 mL capacity and distilled water was added up to the mark. Flask was shaken well to make the solution homogeneous. The solution was tightly enclosed in the dark to ensure to cut off the light radiation.

Preparation of 65% Phosphoric acid

88% of 73.86 mL of phosphoric acid was mixed with water in 100 mL v.f and diluted up to the mark.

Preparation of 10 mL of 10 % starch solution

1g of starch solution was added to 10 mL of water and boiled for 15 minutes.

Preparation of 250 mL of exactly 0.05 N sodium thiosulphate solution

132.9 mL of 0.094 N sodium thiosulphate solution was added into distilled water in 250 mL v.f.

Standardization of sodium thiosulphate solution with standard potassium dichromate solution

Burette was rinsed with distilled water followed by as-prepared sodium thiosulphate solution (approx. 0.1 N) and filled up to the zero mark. 10 cc of standard $K_2Cr_2O_7$ solution was pipetted into a conical flask containing half test tube distilled water. 2 cc of Conc. HCl and one test tube of 5 % KI solution were added. It was covered with a watch glass followed by shaking well, and keeping in dark for about 5 minutes. Watch glass and an inner wall of the conical flask were rinsed with 10 cc of water to trap vaporized I_2 in the solution. It was titrated with sodium thiosulphate solution with constant shaking until faint yellow color appeared. About 2 cc of the starch solution was added when the color of the titrant was like a straw color. Upon addition of starch, the color of the solution was changed to dark blue. This is due to the absorption of iodine by starch solution. More sodium thiosulphate was added drop by drop until the blue color is discharged.

Standardization of iodine solution with standard sodium thiosulphate solution

25.0 mL of iodine solution was pipetted into the 250 mL conical flask and was titrated with standardized sodium thiosulphate solution until the iodine solution is light yellow color. A few drops of the starch indicator were added and titrated and continued dropwise until one drop produces a colorless solution. After calculation, the concentration of iodine was determined to be 0.089 N.

3.9 Characterization of activated carbon

3.9.1 Physicochemical Characterization

As-prepared activated carbon was characterized by methylene blue method and iodine number method for the estimation of methylene blue surface area and posrosity. These are presented below.

Methylene blue Method

The methylene blue adsorption method of activated carbon was determined by batch adsorption experiments. 0.05g of activated carbon was mixed with each 100 mL of different concentrations i.e. 25, 50,100,150,250, and 300 ppm of methylene blue solution, and was agitated for four and half hours in a shaker at 224 rpm and left for about 24 hours. The solution was filtered using Whatman (42) filter paper and the filtrate of the solution was analyzed for residual concentration by using a double beam spectrophotometer (Company: Labtronics).

The amount of methylene blue adsorbed (q_t) uptake per unit mass of the adsorbent (mm/g) at time t is given by the equation

$$q_t = \frac{(C_{o-C_e})V}{W} mg/g \qquad \dots (1)$$

Here C_0 and C_e are initial and equilibrium final concentrations of methylene blue solution in mg/L (ppm), respectively. W is the weight of the adsorbent taken in grams and V is the volume of solution taken in liters (Hayashi et al., 2002).

Iodine number

Iodine number is the amount of iodine in a milligram adsorbed by one gram of carbon. As the size of iodine is small, its size is similar to that of the micro pore range. Therefore, the iodine number indicates the concentration of micropores in the AC.

The 0.1 g of AC was added to each 5 mL of 5 % hydrochloric acid (HCl) in three conical flasks (for triplicate reading) and swirled until all the AC was wetted by acid. The solution was boiled and cooled down to room temperature. To this, 10 mL of 0.1 N iodine solution was added. The solution was shaken thoroughly for 15 minutes using a shaker (220 RPM). Then the solution was allowed to settle and was filtrated using filter paper. The filtrate was titrated against 0.05 N sodium thiosulphate solution. Just after the appearance of the straw yellow color few drops of freshly prepared starch (indicator) were added. The solution becomes dark blue which was titrated against sodium thiosulphate until it becomes colorless. Then the iodine number was determined by using the formula (Rengaraj, n.d.)

$$Iodine\ number = \frac{Amount\ of\ iodine\ in\ (mili\ gram) adsorbed\ by\ carbon}{weight\ of\ carbon\ taken\ in\ gram} mg/g \qquad \dots (2)$$

X-ray diffraction (XRD)

X-ray diffraction analysis (XRD) is a materials science technique for determining a material's crystallographic structure. XRD is a technique that involves irradiating a material with incoming X-rays and then measuring the intensities and scattering angles of the X-rays that exit the substance. The identification of materials based on their diffraction pattern is one of the most common applications of XRD analysis. XRD provides information on how the actual structure differs from the ideal one due to internal stress and flaws, in addition to phase identification (Soares et al., 2003).

X-rays are waves of electromagnetic energy, whereas crystals are regular arrays of atoms. The interaction of incident X-rays with the electrons of crystal atoms scatters incident X-rays. Elastic scattering is the term for this phenomenon, and the electron is the scatterer. The scatterers in a regular array produce a regular array of spherical waves. These waves cancel each other out in most directions due to destructive interference, but they add constructively in a few particular directions, as indicated by Bragg's law (Stanjek & Häusler, 2004).

$$\mathrm{n}\lambda = 2\mathrm{d}\sin\theta \qquad \dots (3)$$

This is called Braggs equation

where, n = order (plane) of reflection (integer number)

λ = wavelength of X-ray

d = interplanar spacing

$\theta =$ angle of incidence

Shimadzu X-ray diffractometer with monochromatic Cu anode and x-ray tube curved graphite filter monochromator (D2 phase Diffractometer, Burker, Germany) at Nepal Academy of Science and Technology (NAST), Khumaltar, Lalitpur was used to investigate the diffraction pattern of activated carbon AC. The sample was prepared by compacting it into aluminium sample holders. XRD data were collected at room temperature, using monochromatic Cu-Kα X- rays (λ = 0.154 nm). The peaks were obtained for different values of 2θ.

Fourier transform-infrared (FTIR) spectroscopy

FTIR (Fourier-transform infrared spectroscopy) is a technique for obtaining an infrared spectrum of a solid, liquid, or gas's absorption or emission. An FTIR spectrometer obtains high-resolution spectral data over a large spectral range at the same time. This gives it a big advantage over a dispersive spectrometer, which only measures intensity over a small range of wavelengths at a time. The Fourier transformation is a decoding procedure that converts a signal from the time domain, where it is a function of retardation, to the frequency domain, where it is a function of frequency (Faix, 1992).

In FTIR spectroscopy, IR radiation was passed through the sample. Some of the infrared radiation was absorbed by the sample and some passed through it (transmitted). The resulting spectrum represented the molecular absorption and transmission, creating a molecular fingerprint of the sample. FT-IR analysis was carried out to find the functional group present in the sample (Chase, 1986).

The oxygen functional groups present on the surface of the sample were identified using FT-IR spectra. FTIR spectra were determined using Perkin Elmer spectrometer 10.6.2 version, located in Amrit Campus Thamel Kathmandu Nepal.

3.7.2 Electrochemical characterization

Cyclic voltammetry measurement

In this experiment, electrochemical characterization of the as-prepared activated carbon was carried out in terms of the cyclic voltammetry measurement. A corroTest Electrochemical Workstation (Wuhan Corrotest Instruments Corp., Ltd.) in the department of Applied Science and Chemical Engineering, Pulchok was used for this measurement.

Figure 5: *Digital image of Potentiostat Workstation at the Department of Applied Science and Chemical Engineering, Pulchok, IOE, TU*

In this experiment, 4 mg of activated carbon was macerated with a small amount of a binder polyvinylidene difluoride (PVDF) in addition to acetylene black. Then the fine paste was dropped on the surface of the carbon glassy electrode from the micropipette. Then the paste over the carbon glassy electrode was dried in the oven.

4 M KOH solution was prepared as a medium of measurement. AC loaded carbon glassy electrode was used as a working electrode, a platinum electrode was used as a counter

electrode and a calomel electrode was used as a reference electrode in a potentiostat workstation using 4 M KOH solution. Cyclic voltammetry was carried out at different scan rate of 1,3,5,10,30 mV/s. The whole work was performed at a potential window of -1.0 V to 0.0 V.

Figure 6: *Digital image of the arrangement of three electrodes in potentiostat for cyclic voltammetry measurement.*

The specific capacitance was calculated using the following relation.

Specific capacitance (C_p) =

$$\frac{\text{Absolute area under the CV curve (AA)}}{2 \times \text{Scan rate (S)} \times \text{Active mass of analyte on CGE (A)} \times \text{Potential window } (\Delta V)}$$

$$Cp = \frac{AA}{2\ S\ A\ \Delta V} \qquad \ldots (3)$$

For the given carbon glassy electrode, the cross-sectional area is 0.070 cm^2.

Mass of the analyte sample = 4 mg.

Electrochemical Impedance spectroscopy measurement

EIS is an AC electrochemical measurement technique which measures the electrical resistance (impedance) of the metal/solution interface over a wide range of frequencies from 1mHz to 10 kHz. The results obtained in EIS spectra are useful to determine polarization resistance (low frequency region), solution resistance (high frequency region) and capacitance of double layer. Electrochemicla impedance spectroscopy was also measured in the potentiostat 3-electrode system (Zive SP 100, Electrochemical Workstation, Korea) at a frequency of 100 kHz to 0.1 Hz at an amplitude of 10 mV per sec.

CHAPTER 4

4. RESULTS AND DISCUSSION

The starting biomass for the preparation of activated carbon was *Shorea robusta* bark. Fine powder of *S. robusta* upon charring with concentrated sulphuric acid produced black mass which is termed as biochar. Dehydration of cellulose or hydrocarbon occurred in charring process with the formation of black residue which is termed as biochar.

Sample (lignin+cellulose+ hemicellulose) + $H_2SO_4 \longrightarrow$ carbon + $H_2SO_4\ xH_2O$

Biochar is a carbon-rich material produced by charing the organic material from agriculture and forestry wastes (also called biomass). Pyrolysis and carbonization of biochar increases the porosity resulting into the higher surface area.

The biochar was pre-carbonized at temperatures (280-300 ℃) in the muffle furnace. At that temperature, some volatile compounds were supposed to be removed with the development of porosity. At that ccarbonization temperature, volatile compounds were also assumed to be lost. Activation made the the raw carbon material porous. In this research work, phosphoric acid was used as activating agent.

The yield of each activated carbon sample produced by chemical activation with phosphoric acid was obtained from calculations. It is calculated as the ratio of the mass of an activated sample after washing and drying to a mass of carbonized sample.

$$\text{Yield (\%)} = \frac{W_c}{W_0} \times 100 \qquad \ldots (4)$$

W_0 = Mass of carbonized sample

W_c = mass of the activated sample after washing and drying

Yield of AC was found to be

yield (%) = $\frac{0.539}{1} \times 100 = 53.9\%$

Determination of λ_{max}

The absorbance was measured by a UV spectrophotometer (Company: Labtronics) in the wavelength window of 300-750 nm. (The maximum absorbance of MB from a plot of absorbance with a concentration in ppm λ_{max} is 660 nm).

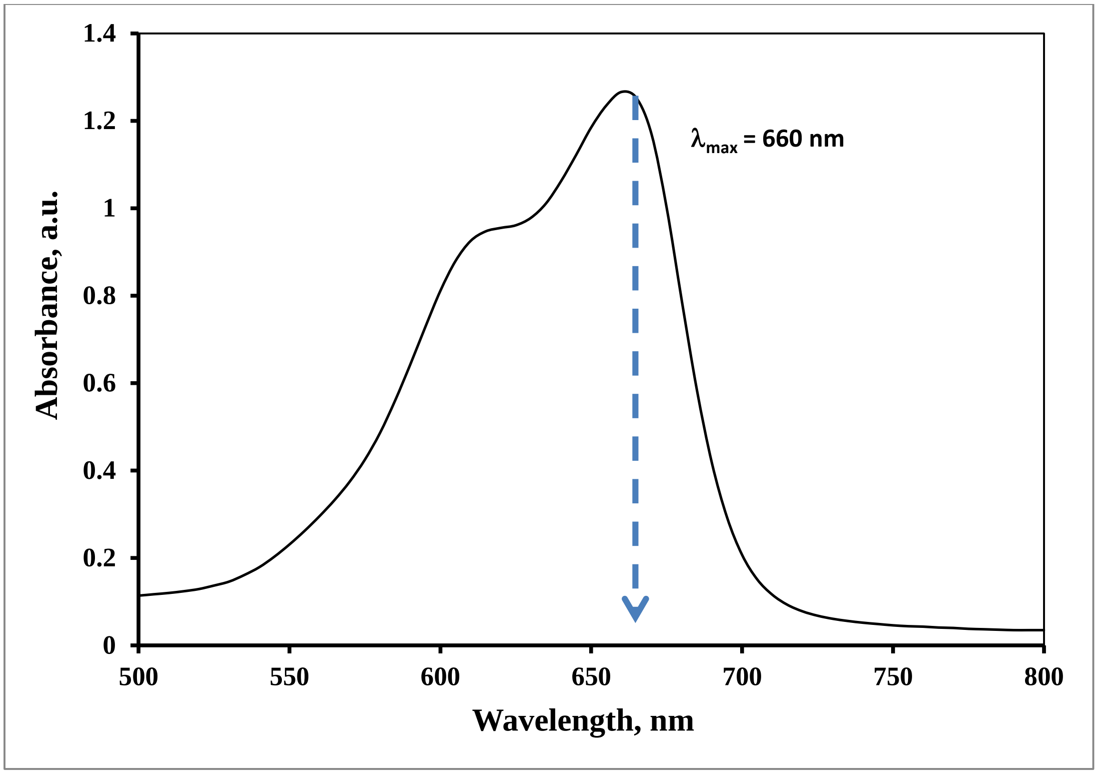

Figure 7: *determination of λmax*

A calibration curve (Standard curve)

The absorbance of 1 to 9 ppm concentration of methylene blue solution was measured by UV visible spectrophotometer and finally plotted curve of absorbance versus concentration.

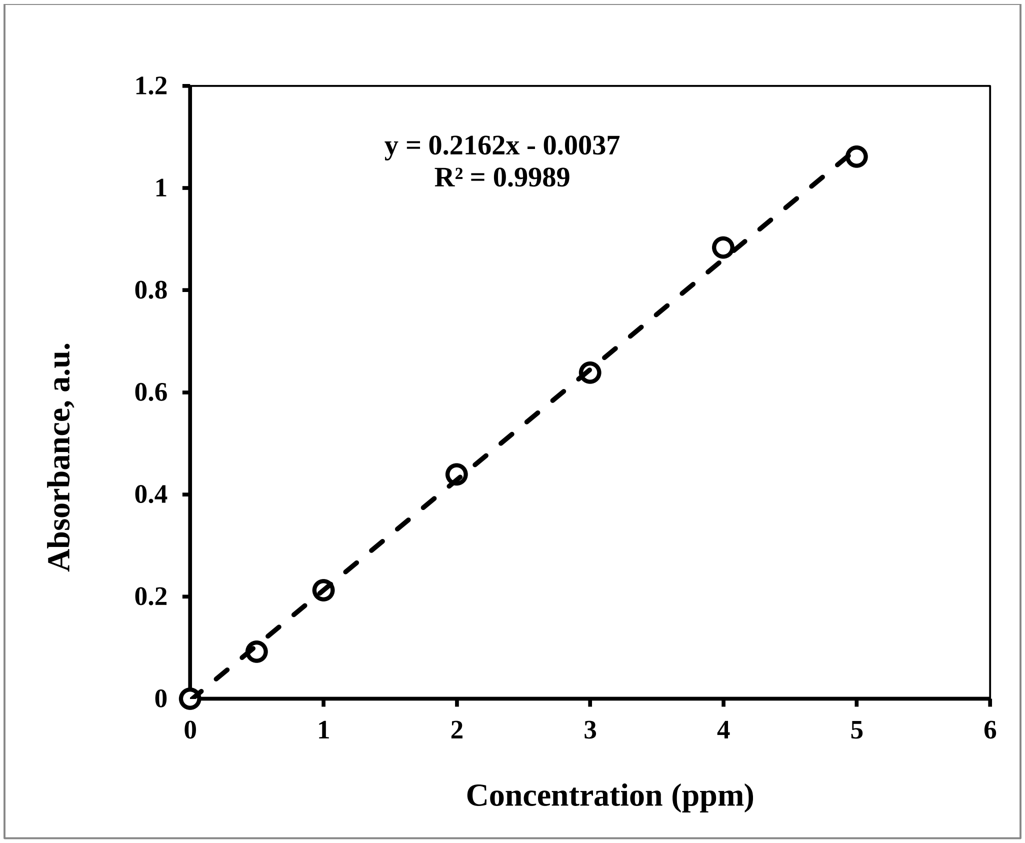

***Figure 8**: Calibration curve for methylene blue solution*

Iodine number

The iodine number gives information about the micropores present in the activated carbon. The iodine number of activated carbons was tabulated in Table. The iodine number of activated carbons ranged from 965.2 to 1384.3 mg/g for the activated carbon prepared by using different concentrations of phosphoric acid (965.2 mg/g is the iodine number of pre-activated char). It was a maximum ratio of 1:5. Activation did not occur entirely with a lower dose of an activating agent. A large amount of activating substance, on the other hand, may disrupt the pore structure. For activated carbon carbonized at temperatures ranging from 300 to 600 °C, the iodine number ranged from 1485.9 to 2108.2 mg/g. At 600 °C temperature complete carbonization occurred. As a result, among all activated carbons carbonized at various temperatures, activated carbon carbonized at 600 °C (AC-600) had the highest iodine number. The presence of a large micropore structure was linked to the greater iodine number value, as well as the higher chance of activated carbon having a large specific surface area due to the enlargement of their pore structure (Saka, 2012).

Table 3: *Iodine number of biochar, pre-activated char, and activated carbon of bark of S. robusta*

SN	Samples	Iodine number (mg/g)
1	Biochar	927.10
2	Pre-activated char	965.20
3	Activated carbon AC-13	1043.00
4	Activated carbon AC-14	1170.00
5	Activated carbon AC-15	1384.30
6	Activated carbon AC-17	1247.14
7	Activated carbon AC-15 at temperature of 300 °C (AC-300)	1485.90
8	Activated carbon AC-15 at temperature of 400 °C (AC-400)	1955.80
9	Activated carbon AC-15 at temperature of 500 °C (AC-500)	2095.50
10	Activated carbon AC-15 at temperature of 600 °C (AC-600)	2108.20

From the above results, it can be seen that the activated carbon AC-15 (carbon: activating agent is 1:5 ratio by mass) has maximum value of iodine number among the test samples and hence taken as optimized sample. Then AC-15 was carbonized at different temperatures. The result shows the micropore present in the AC-15 at 600 ℃ for 3 hours showed the highest value. Whereas the iodine value is minimum for biochar. The biochar could be associated with volatile components and expected with sparse porosity. This study is about the optimization of activating agent dose and optimization of temperature. The ratio of activated carbon to an activating agent AC-15 at 600℃ (AC-600) at 3 hours has an optimized value. The iodine number of the sample is shown on the table 3 and bar diagram 9.

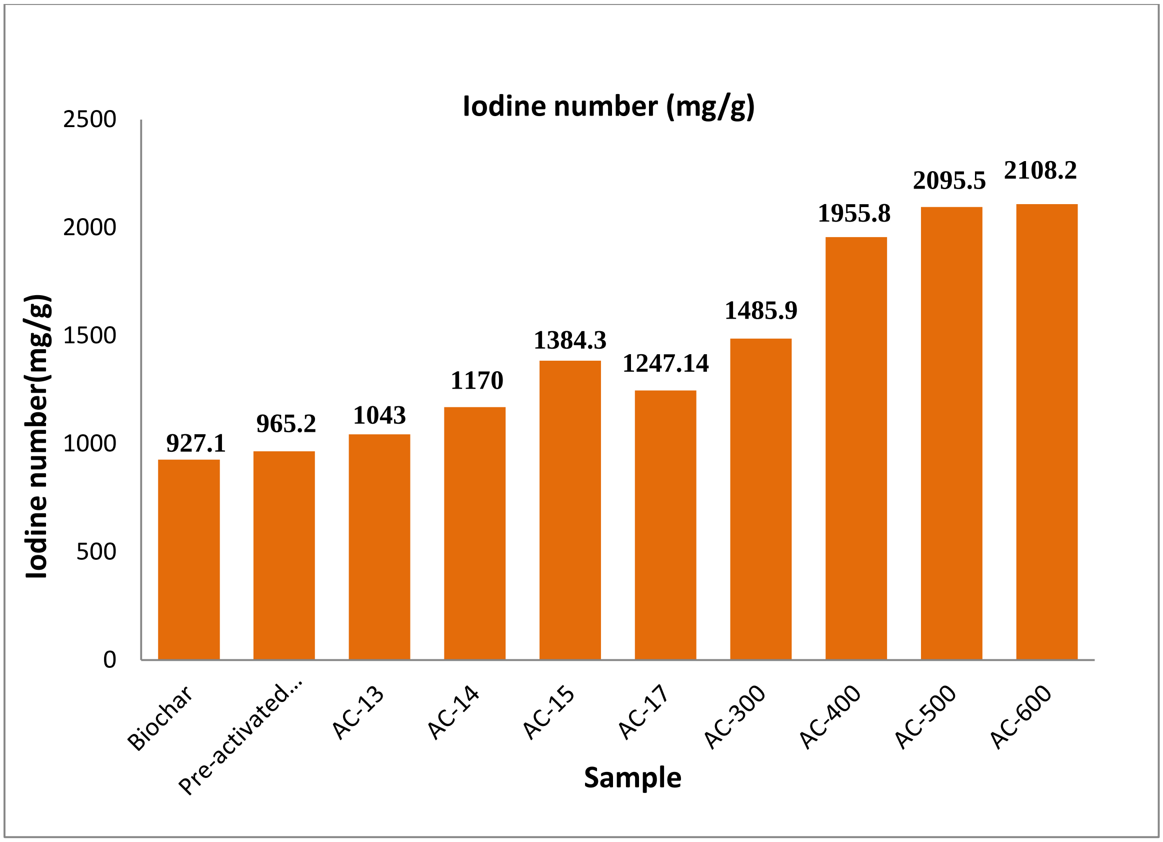

Figure 9: *Iodine number of sample*

Methylene blue adsorption method

The methylene blue (MB) number of biochar and pre-activated-char at 100 ppm of MB solution is 114.31 mg/g and 124.10 mg/g, respectively whereas the MB number of pre-activated-char at 150 ppm of MB solution is 162.08 mg/g and 173.85 mg/g, respectively. For activated carbons produced with various phosphoric acid concentrations, the MB number ranged from 157.56 mg/g to 175.85 mg/g for 100 ppm of MB solution and from 236.12 mg/g to 250.53 mg/g for 150 ppm of MB solution. For the AC-15, the highest value was attained. For activated carbon carbonized at temperatures ranging from 300 to 600 °C, it ranged from 158.67 mg/g to 193.88 mg/g for 100 ppm of MB solution and 207.29 to 264.03 mg/g for 150 ppm of MB solution. Methylene blue adsorption was greatest on activated carbon carbonized at 600 °C. Among all, the activated carbon prepared by using the ratio of phosphoric acid and precursor 1: 5 and carbonized at 600 °C for 3 hours duration had maximum adsorption.

***Table 4**: Methylene blue number of biochar, pre-activate char, and activated carbon of bark of S. robusta at 100ppm of MB solution*

Samples	Ratio	Temperature	Absorbance	Initial conc. (C_0)	Equilibrium conc. (C_e)	MBN (mg/g)
Biochar	-	RT	0.923	100	42.84	114.31
Pre-activated char	-	RT	0.817	100	37.94	124.10
AC-13	1:3	RT		100	21.21	157.56
AC-14	1:4	RT	0.301	100	14.10	171.79
AC-15	1:5	RT	0.257	100	12.07	175.85
AC-17	1:7	RT	0.296	100	13.87	172.25
AC-15-300	1:5	300	0.443	100	20.66	158.67
AC-15-400	1:5	400	0.140	100	6.66	186.67
AC-15-500	1:5	500	0.144	100	6.84	186.30
AC-15-600	1:5	600	0.062	100	3.05	193.88

***Table 5** Methylene blue number of biochar, pre-activated char, and activated carbon of bark of S. robusta at 150 ppm of MB solution*

Samples	Ratio	Temperature	Absorbance	Initial conc (C_0)	Equilibrium conc (C_e)	MBN
Biochar	-	-	0.478	150	63.07	162.08
Pre-activated char	-	-	0.742	150	68.95	173.85
AC-13	1:3	RT	0.687	150	31.93	236.12
AC-14	1:4	RT	0.478	150	22.81	254.37
AC-15	1:5	RT	0.531	150	24.73	250.53
AC-17	1:7	RT	1.364	150	32.90	234.18
AC-15-300	1:5	300	0.999	150	46.35	207.29
AC-15-400	1:5	400	0.764	150	35.49	229.00
AC-15-500	1:5	500	0.524	150	24.40	251.18
AC-15-600	1:5	600	0.385	150	17.98	264.03

Methylene blue adsorption gives information about the adsorption capacity of activated carbon and the methylene blue number (MBN) is used to determine the mesoporosity developed in the AC. The methylene blue number of biochar at 100 and 150 ppm of MB solution is smaller than that of the methylene blue number of pre-activated char. This shows that the mesopore was developed in the pre-activated char is greater than biochar.

Activated carbon produced with various phosphoric acid concentrations, the methylene blue number of AC-15 at 300 °C for 3 hours had maximum MBN. So optimized ratio AC-15 was processed for the optimization of temperature. The methylene blue number of AC-600 at 3 hours had maximum MBN. From all these data, the mesopore present at the activated carbon AC-15 at 600 °C had a maximum.

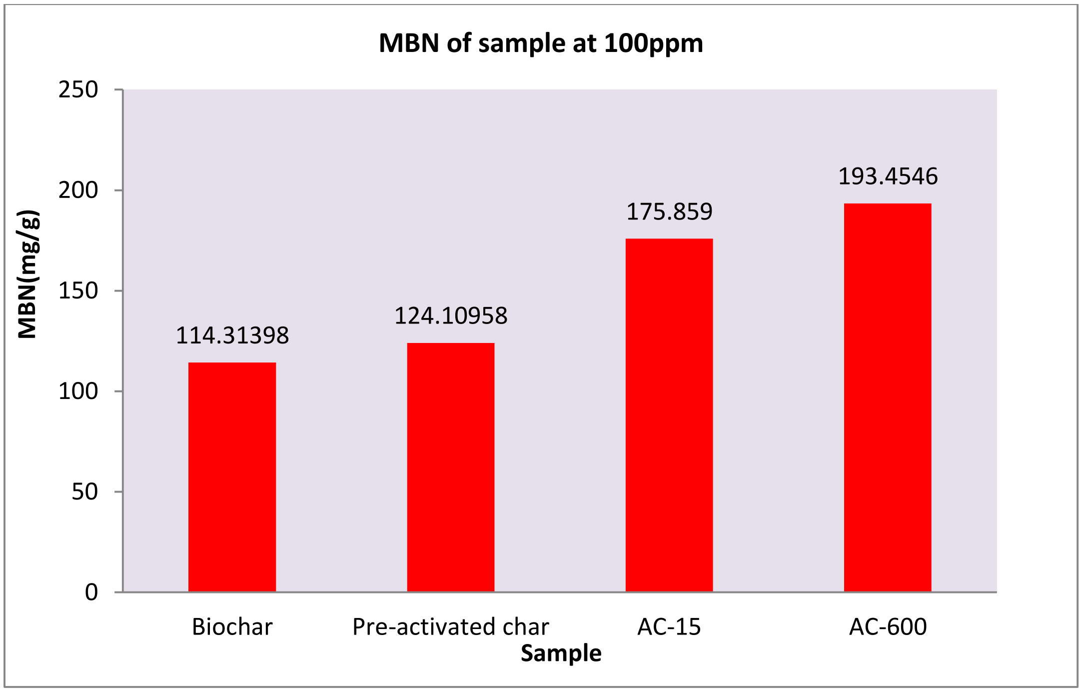

Figure 10: *Methylene blue number of the sample at 100ppm of MB solution*

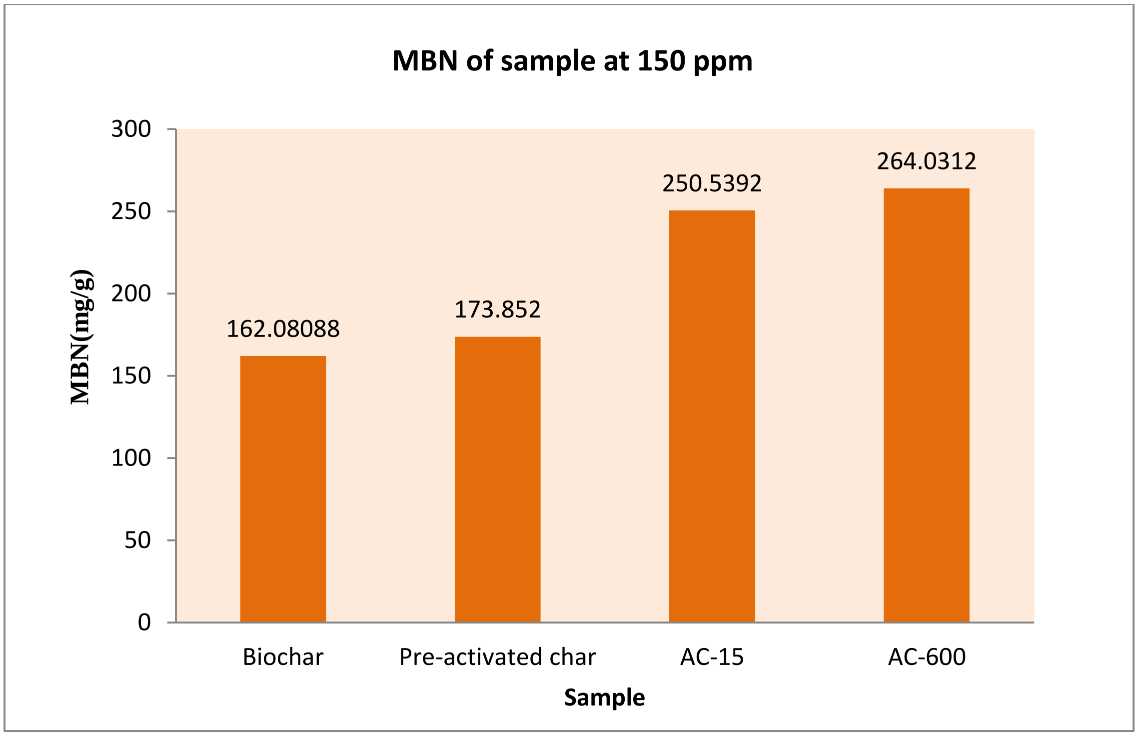

Figure 11: *Methylene blue number of the sample at 150 ppm of MB solution*

X-Ray Diffraction (XRD)

The X-ray diffraction pattern is generally used to study the crystallinity of materials and to calculate the average size of the crystalline. XRD pattern of as-prepared activated carbon (AC-15) at temperatures 400 °C, 500 °C, and 600 °C are shown in the figure below. XRD pattern of AC-400, AC-500, and AC-600 has a broad diffraction peak appearing at about 2θ = 16, 24, and 43. Broad peaks at around 16° are attributable to reflection from the (0 0 2) plane. The (0 0 2) peak denotes the stacking structure of aromatic cellulose layers (Shrestha et al. 2019). Peaks at 26 and 43 could be ascribed to the disordered graphitic (0 0 2) and (1 0 0) planes, respectively. It revealed the creation of a crystalline carbonaceous structure, resulting in improved layer alignment. The peak at around 26 was caused by the stacking structure of aromatic carbon layers. The broad peaks at around 20-30 could be the presence of amorphous nature of carbon. The AC is amorphous similar to commercially AC and poorly graphitized (Ma & Ouyang, 2013). Some insignificant peaks could be seen, which may be due to the presence of some impurities or moisture associated with the sample It is common to have some shoot off peak due to activating agent impurities.

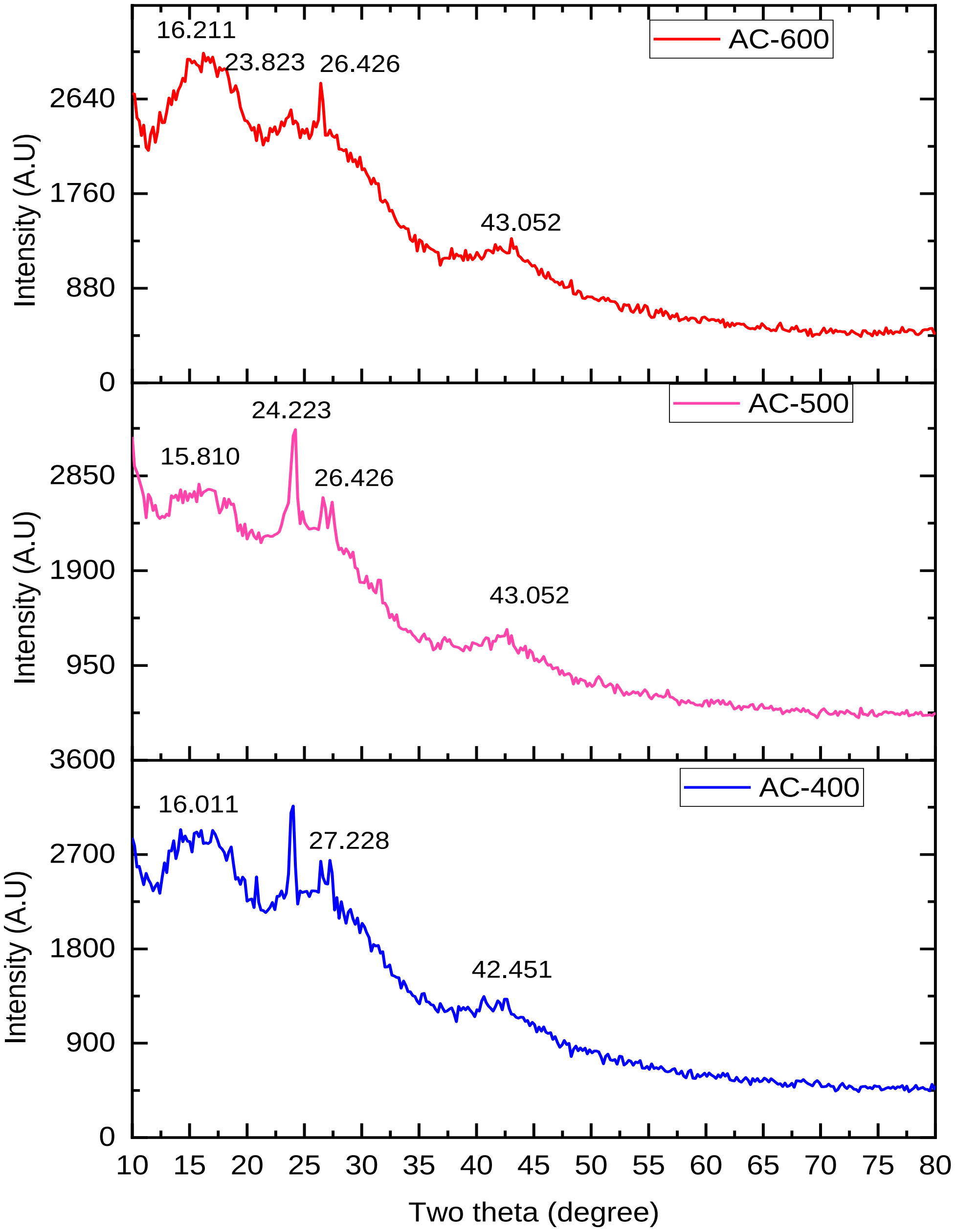

Figure 12: Combined XRD pattern of AC-400, AC-500, and AC-600

FTIR spectrum of pre-activated char and activated carbon

FTIR (Fourier Transform Infrared Spectroscopy) spectra were obtained to better understand the nature of functional groups on the surface of the bark of *S. robusta* powder. FTIR spectrum of AC of *S. Robusta* was recorded by PerkinElmer Spectrum (IR Version 10.6.2) FTIR spectrometer present in Department of chemistry Amrit Campus.

Figure 4.7 shows the FTIR spectra of pre-activated char and activated carbon. The spectrum showed a broad peak around 3400 cm^{-1} which is due to stretching. Of -O-H group which could be associated with the remnant of different polyphenol and acids. The hydroxyl groups are mostly associated with the cellulosic component, which is the primary component of lignocellulosic materials (Gomez-Serrano et al., 1996). The band at low-frequency values implies that the hydroxyl groups are involved in hydrogen bonding. For alcohols, phenols, and carboxylic acids, the position of the band due to non-bonded OH groups is usually above 3500 cm^{-1}. The band at 1600-1400 cm^{-1} is due to the aromatic C-C bond and various substitution modes of an aromatic ring. So peak at 1582 cm^{-1} and 1447 cm^{-1} was attributed to aromatic C-C stretching (Shin et al., 1997). The peak at 1163 cm^{-1} is attributed to the phenol C-O stretching (Shin et al., 1997)**.** The peaks at 688 and 560cm^{-1} are assigned to the bending mode of aromatic compounds. The region between 700 to 900 cm^{-1} contains various bands related to aromatic. The additional peak at 679, 596, and 535 cm^{-1} can be assigned to the bending mode of aromatic compounds (Jain et al., 2010). A few changes were observed in FTIR spectra of pre-activated char after activation with orthophosphoric acid.

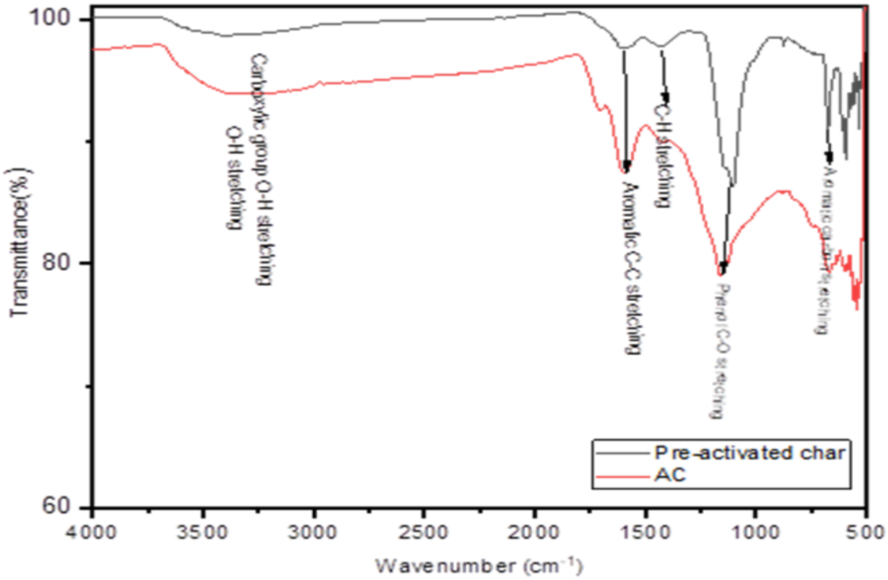

Figure 13: FTIR spectrum of Pre-activated char and activated carbon

Cyclic voltammetry Measurement

Cyclic voltammetry of AC-400 and AC-500 were measured to study the electrochemical performance. Result shows that, the AC-500 exhibited good indication for double layer capacitance. In the current-potential curve, the current is high for small change in potential for AC-500 and is expected to exhibit good charge storage upon charging and discharging. The absolute area under the CV curve found was 3.2200688523973E-4 and 1.8401302101665E-4 for AC-500 and AC-400 at a scan rate of 3 mV/s. The current of CV was in the range of milliampere range which indicates the possible application of such carbon materials for electrochemical applications. Furthermore, the nature of CV shows that AC-500 could be used for electrical double-layer capacitor (EDLC) applications. Its application is also supported by a methylene blue number value of 175.859 mg/g and an iodine number value of 2095.5 mg/g.

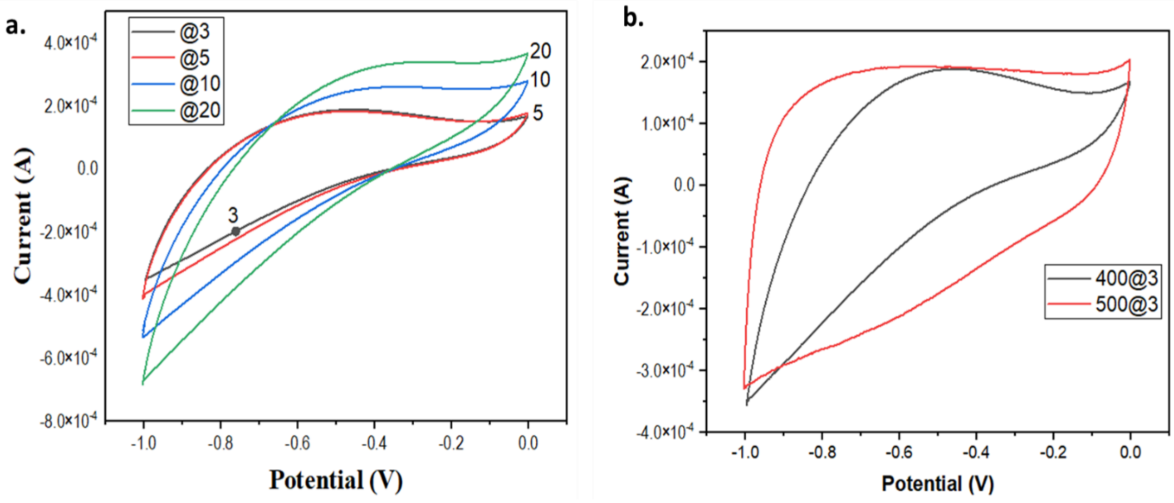

Figure 14: *(a) A cyclic voltammetry curve of AC-400 at different scan rates (3, 5, 10, 20 mV/s), (b) A cyclic voltammetry curve of AC-400 and AC-500 at the scan rate of 3 mV/s*

Specific capacitance (C_p) =

$$\frac{\text{Absolute area under the CV curve (AA)}}{2 \times \text{Scan rate (S)} \times \text{Active mass of analyte on CGE (A)} \times \text{Potential window } (\Delta V)}$$

$$Cp = \frac{AA}{2\ S\ A\ \Delta V}$$

For the given carbon glassy electrode, the cross-sectional area is 0.070 cm^2.

$$Cp = \frac{1.8401 \times 10^{-4}}{2 \times (3 \times 10^{-3}\ V/s) \times 0.0004\ g \times 1\ V}$$

$$= 76.67\ \text{Farad/g}$$

Besides this method, specific capacitance of the as-synthesized activated carbon can be calculated from galvanic charge-discharge curve. However, due to the limitation of instruement availability and time constraints, specific capacitance from galvanic charge discharge (GCD) has not been calculated.

EIS measurement

EIS data are generated by measuring the current response and hence recording the phase shift and amplitude change over a range of applied frequencies under the application of AC potential to the potentiostat. Study of current response over a range of frequencies allows the separation of electrochemical process occurring at different time scales, making it ideal for separating electronoic and ionic processes in the mixed conductor. The result shows, the high Rct value of AC-15 at 500 °C. A higher value of charge transfer resistance indicates the higher difficulty encountered when an electron moves from one chemical species to another chemical species. The result shows that AC-15 at 500 °C is good for double layer capacitance in energy storage.

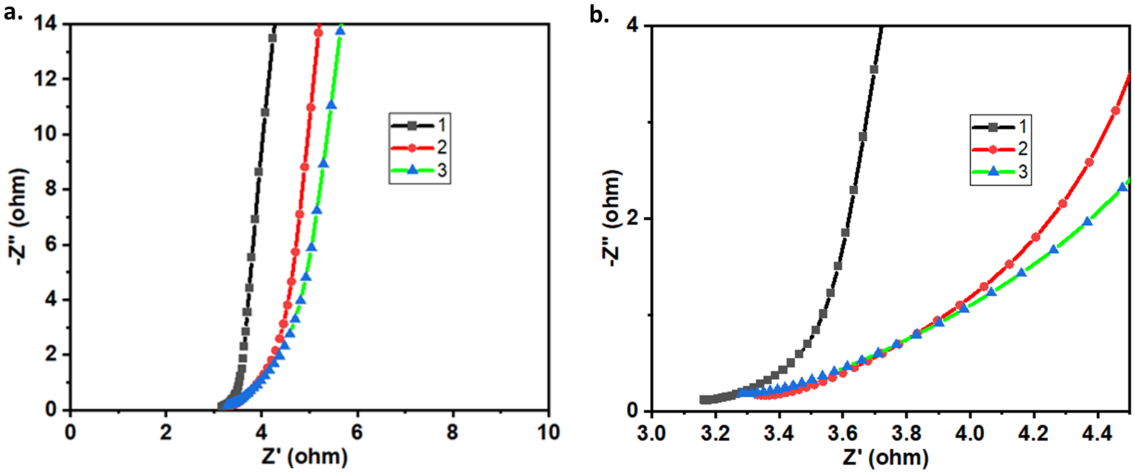

***Figure 15**: Electrochemical impedance spectroscopy for (1) AC-500 (2) AC-400 (3) AC-300. Figure a. is for a wide range of EIS spectra and figure b is for highlight of the spectra a.*

CHAPTER 5

5. CONCLUSIONS AND SUGGESTIONS

Activated carbons (ACs) were successfully prepared from *S. robusta* bark by charring it with conc. sulphuric acid and treating it with varying doses of orthophosphoric acid at varying temperatures for 3 hours in a muffle furnace. The iodine number and methylene blue number of activated carbons were determined. Further characterization of activated carbon was done by XRD and FTIR. The broad peaks at around 20-30 could be the presence of the amorphous nature of carbon. The AC is amorphous similar to commercially AC and poorly graphitized.

Finally, AC-400 and AC-500 were taken for measurement of cyclic voltammetry. Concluding results are presented below

1. AC-15 exhibited the highest value of iodine number. The determined value of iodine number for the case was 1384.30 mg/g. Then this sample was optimized for further study. The iodine number got increased with incrasing temperature and was found to be 2095.50 mg/g for AC-15 at 500 °C.
2. The methylene blue number of AC-15 was found highest and was recorded as 175.85 mg/g. The value got increased with increased temperature and was recorded 186.30 mg/g at 500 °C.
3. In the study of electrochemical analysis, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were studied. The AC-15-500 gave good cyclic voltammetry out of AC-15 heated for 3 h at 300, 400, and 500 °C. The charge transfer coefficient (Rct) value was found highest for AC-15 heated at 500 °C.
4. The specific capacitance calculated for AC-15 at 500 °C was 76.67 Farad/g. Furthermore, the nature of CV shows that AC-500 could be used for electrical double-layer capacitor (EDLC) applications

Suggestions for further work

- In this study activated carbon was prepared from *Shorea robusta* bark by charring with conc. sulphuric acid and is activated with phosphoric acid with different ratios of precursor to an activating agent with different activating temperatures for a fixed time. The effect of carbonization time was not studied yet.

- In this study activated carbon was prepared by charring with conc. sulphuric acid. AC can also be prepared from direct carbonization of *Shorea robusta* bark at a temperature of about 800-900°C.
- Optimization of further work such as activation of AC by heating the sample in tube furnace can enhance the further surface area and can increase the specific surface area.

REFERENCES

Abdollahi, M., & Hosseini, A. (2014). Charcoal. In P. Wexler (Ed.), *Encyclopedia of Toxicology (Third Edition)* (pp. 779–781). Academic Press. https://doi.org/10.1016/B978-0-12-386454-3.00685-0

Adhikari, M. P., Adhikari, R., Shrestha, R. G., Rajendran, R., Adhikari, L., Bairi, P., Pradhananga, R. R., Shrestha, L. K., & Ariga, K. (2015). Nanoporous activated carbons derived from agro-waste corncob for enhanced electrochemical and sensing performance. *Bulletin of the Chemical Society of Japan*, *88*(8), 1108–1115.

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.

Barker, M. E. (1930). The Mechanism of Charcoal Activation. *Industrial & Engineering Chemistry*, *22*(9), 926–931. https://doi.org/10.1021/ie50249a009

Chase, D. Bruce. (1986). Fourier transform Raman spectroscopy. *Journal of the American Chemical Society*, *108*(24), 7485–7488. https://doi.org/10.1021/ja00284a007

Faix, O. (1992). Fourier Transform Infrared Spectroscopy. In S. Y. Lin & C. W. Dence (Eds.), *Methods in Lignin Chemistry* (pp. 83–109). Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-642-74065-7_7

Ghosh, S., Santhosh, R., Jeniffer, S., Raghavan, V., Jacob, G., Nanaji, K., Kollu, P., Jeong, S. K., & Grace, A. N. (2019). Natural biomass derived hard carbon and activated carbons as electrochemical supercapacitor electrodes. *Scientific Reports*, *9*(1), 16315. https://doi.org/10.1038/s41598-019-52006-x

Gomez-Serrano, V., Pastor-Villegas, J., Perez-Florindo, A., Duran-Valle, C., & Valenzuela-Calahorro, C. (1996). FT-IR study of rockrose and of char and activated carbon. *Journal of Analytical and Applied Pyrolysis*, *36*(1), 71–80. https://doi.org/10.1016/0165-2370(95)00921-3

Gurten Inal, I. I., & Aktas, Z. (2020). Enhancing the performance of activated carbon based scalable supercapacitors by heat treatment. *Applied Surface Science*, *514*, 145895. https://doi.org/10.1016/j.apsusc.2020.145895

Hayashi, J., Horikawa, T., Muroyama, K., & Gomes, V. G. (2002). Activated carbon from chickpea husk by chemical activation with K2CO3: Preparation and characterization. *Microporous and Mesoporous Materials*, *55*(1), 63–68. https://doi.org/10.1016/S1387-1811(02)00406-7

Hayashi, J., Kazehaya, A., Muroyama, K., & Watkinson, A. P. (2000). Preparation of activated carbon from lignin by chemical activation. *Carbon*, *38*(13), 1873–1878. https://doi.org/10.1016/S0008-6223(00)00027-0

Jain, M., Garg, V. K., & Kadirvelu, K. (2010). Adsorption of hexavalent chromium from aqueous medium onto carbonaceous adsorbents prepared from waste biomass. *Journal of Environmental Management*, *91*(4), 949–957. https://doi.org/10.1016/j.jenvman.2009.12.002

Joshi, S., Shrestha, R. G., Pradhananga, R. R., Ariga, K., & Shrestha, L. K. (2022). High Surface Area Nanoporous Activated Carbons Materials from Areca catechu Nut with Excellent Iodine and Methylene Blue Adsorption. *C*, *8*(1). https://doi.org/10.3390/c8010002

Joshi, S., Shrestha, S., & Shrestha, B. (2021). Activated Carbon from Various Agricultural Wastes by H3PO4 Activation: Preparation and Characterization. *Chemical Engineering & Technology*, *44*(12), 2327–2332. https://doi.org/10.1002/ceat.202000327

Lee, T., Ooi, C.-H., Othman, R., & Yeoh, F.-Y. (n.d.). *ACTIVATED CARBON FIBER - THE HYBRID OF CARBON FIBER AND ACTIVATED CARBON*. 19.

Ma, X., & Ouyang, F. (2013). Adsorption properties of biomass-based activated carbon prepared with spent coffee grounds and pomelo skin by phosphoric acid activation. *Applied Surface Science*, *268*, 566–570. https://doi.org/10.1016/j.apsusc.2013.01.009

Najm, I. N., Snoeyink, V. L., Lykins, B. W., & Adams, J. Q. (1991). Using Powdered Activated Carbon: A Critical Review. *Journal - American Water Works Association*, *83*(1), 65–76. https://doi.org/10.1002/j.1551-8833.1991.tb07087.x

Rautiainen, O. (1999). Spatial yield model for Shorea robusta in Nepal. *Forest Ecology and Management*, *119*(1), 151–162. https://doi.org/10.1016/S0378-1127(98)00519-2

Rengaraj, S. (n.d.). *Preparation and characterisation of acti vated carbon from agricultural wastes*. 4.

Saka, C. (2012). BET, TG–DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with ZnCl2. *Journal of Analytical and Applied Pyrolysis*, *95*, 21–24. https://doi.org/10.1016/j.jaap.2011.12.020

Shin, S., Jang, J., Yoon, S.-H., & Mochida, I. (1997). A study on the effect of heat treatment on functional groups of pitch based activated carbon fiber using FTIR. *Carbon*, *35*(12), 1739–1743. https://doi.org/10.1016/S0008-6223(97)00132-2

Shrestha, D., Gyawali, G., & Rajbhandari, A. (2018). Preparation and characterization of activated carbon from waste sawdust from saw mill. *Journal of Institute of Science and Technology*, *22*(2), 103–108.

Shrestha, D., Maensiri, S., Wongpratat, U., Lee, S. W., & Nyachhyon, A. R. (2019). Shorea robusta derived activated carbon decorated with manganese dioxide hybrid composite for improved capacitive behaviors. *Journal of Environmental Chemical Engineering*, *7*(5), 103227.

Shrestha, D., & Rajbhandari, A. (2021). The effects of different activating agents on the physical and electrochemical properties of activated carbon electrodes fabricated from wood-dust of Shorea robusta. *Heliyon*, *7*(9), e07917.

Shrestha, L. K., Shrestha, R. G., Maji, S., Pokharel, B. P., Rajbhandari, R., Shrestha, R. L., Pradhananga, R. R., Hill, J. P., & Ariga, K. (2020). High surface area nanoporous graphitic carbon materials derived from lapsi seed with enhanced supercapacitance. *Nanomaterials*, *10*(4), 728.

Silva, L. A. da, Borges, S. M. S., Paulino, P. N., Fraga, M. A., Oliva, S. T. de, Marchetti, S. G., & Rangel, M. do C. (2017). Methylene blue oxidation over iron oxide supported on activated carbon derived from peanut hulls. *Discovering New Routes for Sustainable Development*, *289*, 237–248. https://doi.org/10.1016/j.cattod.2016.11.036

Sim, C.-K., Majid, S. R., & Mahmood, N. Z. (2015). Electrochemical performance of activated carbon derived from treated food-waste. *International Journal of Electrochemical Science*, *10*(12), 10157–10172.

Soares, P. C., Zanotto, E. D., Fokin, V. M., & Jain, H. (2003). TEM and XRD study of early crystallization of lithium disilicate glasses. *Journal of Non-Crystalline Solids*, *331*(1), 217–227. https://doi.org/10.1016/j.jnoncrysol.2003.08.075

Soleimani, M., & Kaghazchi, T. (2007). Agricultural Waste Conversion to Activated Carbon by Chemical Activation with Phosphoric Acid. *Chemical Engineering & Technology*, *30*(5), 649–654. https://doi.org/10.1002/ceat.200600325

Soni, R. K., Dixit, V., Irchhaiya, R. I., & Singh, H. (2013). A Review Update on Shorea robusta Gaertn f. (Saal). *Journal of Drug Delivery and Therapeutics*, *3*(6), 127–132. https://doi.org/10.22270/jddt.v3i6.653

Stanjek, H., & Häusler, W. (2004). Basics of X-ray Diffraction. *Hyperfine Interactions*, *154*(1–4), 107–119. https://doi.org/10.1023/B:HYPE.0000032028.60546.38

Thambidurai, A., Lourdusamy, J. K., John, J. V., & Ganesan, S. (2014). Preparation and electrochemical behaviour of biomass based porous carbons as electrodes for supercapacitors—A comparative investigation. *Korean Journal of Chemical Engineering*, *31*(2), 268–275. https://doi.org/10.1007/s11814-013-0228-z

Yue, Z., & Economy, J. (2017). 4—Carbonization and activation for production of activated carbon fibers. In J. Y. Chen (Ed.), *Activated Carbon Fiber and Textiles* (pp. 61–139). Woodhead Publishing. https://doi.org/10.1016/B978-0-08-100660-3.00004-3

Tadda, M., Ahsan, A., Shitu, A., ElSergany, M., Arunkumar, T., Jose, B., . . . Research. (2016). A review on activated carbon: Process, application and prospects. *Journal of Advanced Civil Engineering Practice and Research, 2*(1), 7-13.

Taer, E., Gultom, E. S., Agustino, Taslim, R., & Febriani, W. (2021). Less Expensive and Eco-Friendly Preparation of Activated Carbon Derived from Coffee Leaf as an Supercapacitors Electrode. *Journal of Physics: Conference Series*, *2049*(1), 012019. https://doi.org/10.1088/1742-6596/2049/1/012019

Taer, E., Yusra, D. A., Amri, A., Taslim, R., & Putri, A. (2021). The synthesis of activated carbon made from banana stem fibers as the supercapacitor electrodes. *Materials Today: Proceedings, 44,* 3346–3349.

Tan, X.-f., Liu, S.-b., Liu, Y.-g., Gu, Y.-l., Zeng, G.-m., Hu, X.-j., . . . Jiang, L.-h. (2017). Biochar as potential sustainable precursors for activated carbon production:

Multiple applications in environmental protection and energy storage. *Bioresource Technology*, *227*, 359-372. doi:https://doi.org/10.1016/j.biortech.2016.12.083

Williams, P. T., Reed, A. R. J. B., & Bioenergy. (2006). Development of activated carbon pore structure via physical and chemical activation of biomass fibre waste. *30*(2), 144-152.

Zhang, Q.-Z., Zhang, D., Miao, Z.-C., Zhang, X.-L., & Chou, S.-L. (2018). Research progress in mno2–carbon based supercapacitor electrode materials. *Small*, *14*(24), 1702883. doi:https://doi.org/10.1002/smll.201702883