Microwave-assisted synthesis and characterization of biomass-derived porous carbon from natural precursors *Plumeria pudica* and *Tecoma capensis* leaves

P. SANGEETHA

20PCH018

Thesis Submitted to

Avinashilingam Institute for Home Science and Higher Education for Women,

Coimbatore-641 043

In Partial Fulfillment of the Requirements for the Degree of

Master of Science in Chemistry

May, 2022

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Supervisor

26/5/2022

Signature of the

Head of the Department

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P.SANGEETHA

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LIST OF ABBREVIATION

PCC	Pre-carbonized carbon
AC	Activated carbon
PC-PPL	Pre-carbonized *Plumeria pudica* leaves
AC-PPL	Activated *Plumeria pudica* leaves
PC-TCL	Pre-carbonized *Tecoma capensis* leaves
AC-TCL	Activated *Tecoma capensis* leaves
UV	Ultra Violet
FT-IR	Fourier Transform Infrared Spectroscopy
XRD	X-Ray Diffraction
TGA	Thermo Gravimetric Analysis
DTA	Differential Thermal Analysis

1. INTRODUCTION

High performance energy storage devices have attracted much attention in the past few decades, driven by the increasing challenges of worldwide energy crisis and environmental pollution and the growing market demands for portable electronic devices **(Ning Zhao *et al.*, 2020)**.Currently, the main energy storage systems are batteries, in which the energy can be stored electrochemically and the chemical reactions can release the energy in terms of electrical carriers which can be extracted to the external circuit. **(Kasinath ojha *et al.*, 2017)**. However, Supercapacitors have drawn much more attention than batteries because of their fast storage capability (i.e, low discharge time: Sc: 1-10 S Vs. lithium ion battery: 10-60 min) and enhanced cyclic stability (Sc >30,000 h Vs battery > 500h) **(Waseem Raza *et al.*, 2018).**

Supercapacitors contain current collector, electrode, electrolyte, Separator etc., among which electrode materials play a vital role in determining the capacitive performance of supercapacitors. The mainly used electrode materials are electrical conductive polymer (polyaniline, poly (3,4-ethylenedioxythiophene), carbon based material (activated carbon, graphene and carbon nanotube) and transition metal oxide based material (MnO_2, NiO and Fe_3O_4). Currently, more than 80% of the commercially manufactured supercapacitors make use of carbon as electrode material with respect to high performance of supercapacitors, it is highly desirable that carbon materials possess high specific surface area, hierarchical porous structure (combination of macro-, meso-,and micro-pores), and heteroatom doping (incorporation of B, N, P, and O into the carbon lattice) which enhances the capacitance of carbon materials. **(Yong-Qing Zhao *et al.*, 2016).**

1.1 Classification and applications of supercapacitors:

Based on energy storage mechanism, supercapacitor are classified into i) electric double-layer capacitor (EDLC) that store and release energy based on electrode-electrolyte interface, ii) pseudocapacitor that owing to the rapid faradaic reactions occurring at the electrode-electrolyte interface and iii) hybrid supercapacitor that combining the properties of EDLC and pseudocapacitor **(Jingjing *et al.*, 2020)**. Compared to pseudocapacitor and hybrid supercapacitor, EDLC is mainly based on carbon materials as an electrode. The high surface area of carbon

materials is ultimately responsible for their excellent capacitance, therefore, the use of carbon based materials as the electrode materials for EDLC has provided a breakthrough in energy storage (high capacitance) **(Waseem Raza *et al.*, 2018)**

Currently, supercapacitors are widely used in consumer electronics, memory backup systems and industrial power and energy management. A more recent application is the use of supercapacitors in emerging doors on the Airbus A380, highlighting their safe and reliable performance. **(Li Li Zhang *et al.*, 2009)**

1.2 Carbon based electrode materials:

Carbon is an essential constituent of the world and all living organisms and it is the fourth most abundant element and second most common element in the human body. It has many forms of allotropes, which are widely used in many fields. **(Sumair Imtiaz *et al.*, 2016)**

In recent years, carbon materials have received significant research attention, because of their potent applications in energy storage and environmental monitoring as they have unique properties such as easy availability, nontoxicity and environmental friendliness **(Shaofeng zhou *et al.*, 2019)**. There are various carbon materials ranging from 0 dimensional to 3 dimensional materials like fullerene, carbon nanotubes, graphenes, activated carbons, carbon aerogels, templated porous carbon etc., that have been successfully tried as electrode for supercapacitors due to good electrical conductivity. **(Li wang *et al.*, 2014)**

Among them, Carbonaceous materials with porous structure have been regarded as promising electrode materials for supercapacitors due to their inherent advantage such as abundant pore structure, adjustable pore diameters and high heat resistance. **(Lang Huang *et al.*, 2020)** The pores can be divided into three types based on their pore size such as macropores (>50 nm), mesopores (2-50 nm) and micropores (<2nm) **(Lin Qian *et al.*, 2020)**.

1.2.1 Activated carbon:

Activated carbon is also known as activated charcoal which is porous carbon materials with high amorphous, low crystalline nature and large internal surface area. It has a microcrystalline and non-graphitic form of carbon. Non-graphitic form means a matter that consists of a small amount of hydrogen or a large amount of oxygen in the structure. It has high

performance in electrical conductivity, good thermal stability as well as surface reactivity that becomes the main reason why activated carbon has been widely used in recent years **(Mohd Adib yahya *et al.*, 2018)**. Activated porous carbon has great interest for utilization as supercapacitor electrodes because they can be readily prepared from cheap biomass residues and wastes. Activated carbons prepared from rice husk, pistachio shells, bamboo, banana fibers, waste coffee grounds, cassava peel waste, sugarcane bagasse, willow catkin, tobacco etc., have been successfully tried as electrodes for supercapacitors. **(Youliang cheng *et al.*, 2020)**

Picture courtesy: (https;//m.indiamart.com/proddetail/activated-carbon-2675235048.html)

Fig: 1.1 Activated carbon with hierarchical pore structure

1.2.2 Precursors for activated carbon:

Carbon precursors with high carbon content like fossil fuels, polymers and biomass materials are usually used to produce activated carbon. Among them, the biomass derived carbon materials have attracted much attention because of their abundant source, easy availability and renewable nature. Biomass is a general term that encompasses both phytomass (plant biomass) and Zoomatoss (animal biomass) containing chemical energy converted from solar energy initially via the plant metabolism process well known as photosynthesis **(Minjun Kim *et al.*, 2020)**. Among them, the plant biomass, including stems, seeds, leaves of various plant species, are of particular interest because they are cheap, easily available and environmentally friendly because renewable energy sources are at the forefront because they provide clean and green energy. Therefore, conversion of renewable biomass into porous carbon has attracted plenty of attention in various energy-related applications. **(Gaoxin Lin *et al.*, 2017)**.

Fig: 1.2 Conversion of biomass waste into energy (Zhihong *et al.*, 2013)

1.3 Preparation of Activated carbon:

Production of activated carbon involves two important steps which are carbonization of biomass waste at high temperature to produce carbon samples and activation of biomass produced carbon samples with appropriate activating agents at high temperature under inert environment to enlarge the specific surface area by creating the hierarchical pores on the carbon surface, resulting in the high performance supercapacitors. **(Rajesh kumar *et al.*, 2020)**

1.3.1 Carbonization:

The synthesis of activated carbon from biomass generally starts with pre-treatment of the sample, including crushing, drying and sieving to obtain small particles within a specific size range and this is followed by carbonization of biomass. Carbonization or pyrolysis is the thermal decomposition of raw materials in a furnace in an inert atmosphere in order to remove volatile, non-carbon species like nitrogen, oxygen and hydrogen and to enhance fixed carbon content in order to produce biochar.**(Sumon Reza *et al.*, 2020)** The products from this process are charcoal when it is used as fuel, biochar when used as fertilizer, biocoke for metal extraction and finally activated carbon when regular charcoal is upgraded for adsorption process and purification purposes. The pyrolysis parameters significantly affect the process and highly influence the quality of final products. Carbonization temperature is one of the most important parameters which has a significant effect on the process, followed by heating rate, amount of inert gas and its flow rate and finally the carbonization residence or holding time.

1.3.2 Types of carbonization:

i) Low-temperature carbonization:

This process occurs between 300 and 400°C. During this stage the decomposition of hemicellulose and cellulose will take place. The biomass structure keeps breaking and decomposing to produce slightly richer fixed carbon content. **(Mahmoud Amer *et al.*, 2020)**

ii) High-temperature carbonization:

If heating continues over 400°C a very-high carbon rich charcoal is obtained.

Generally, high temperature carbonization (600-700°C) results in reduced yield of char while increasing the liquid and gasses release rate. It will also increase ash and fixed carbon content and lower the amount of volatile matter. **(Norhusna Mohamad Nor *et al.*, 2013)**

1.3.3 Stages of carbonization:

Carbonization process can be classified into four phases depending on the temperature of each stage. In phase 1, the temperature < 200°C involves initial drying of raw material. In phase 2, the temperature is between 170-300°C, which involves the pre-carbonization phase, which produces small amounts of pyroligneous liquids and non-condensable gasses. In phase 3, the temperature is between 250-300°C which involves elimination of a large proportion of pyroligneous liquids and tars produced in phase 2, producing charcoal. In phase 4, the temperature is more than 300°C, which increases the carbon content of the charcoal by diffusing any remaining volatile matter content.

1.3.4 Hydrothermal carbonization:

Recently, the use of hydrothermal carbonization is gaining popularity in activated carbon synthesis. In this method, the biomass is mixed with water or reagent solution prior to carbonization. **(Syieluing Wong *et al.*, 2018)**. The product obtained from hydrothermal carbonization is known as hydrochar.

Hydrochar with a rich oxygenated functional group is a highly value-added carbonaceous material, which is produced by the thermochemical conversion, at the temperature range of 150-350°C, under autogenous pressure. **(Shicheng zhang *et al.*, 2019)** Usually the reaction pressure

is not controlled in the process and is autogenic with respect to saturation vapor pressure of water corresponding to the reaction temperature.

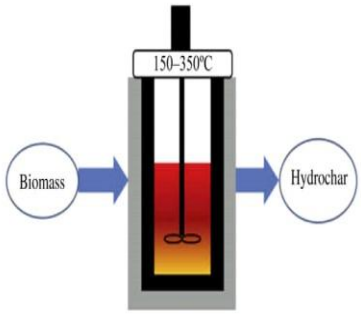


Fig: 1.3 Hydrothermal carbonization (Shicheng zhang *et al.*, 2019)

During this process, the biomass materials first decompose into smaller monomers and then complex reactions related to dehydration, polymerization and aromatization occur. **(Lin Qian *et al.*, 2020)** Below 200°C, the porosity of the hydrocarbon increases with the operating temperature, while the surface area and porosity decrease by further increase in temperature due to increasing degree of aromatization. **(Lulu Lyu *et al.*, 2019)**

A post high temperature activation is generally employed to further enrich porosity, tune the microstructure and enhance the graphitization degree of biochar.

1.4 Activation of Carbon:

Activation is a key step to enhance the pore structure. After carbonization of biomass, physical or chemical activations are required to activate the carbonized material. **(Syieluing wong *et al.*, 2018)** In the activation process, the oxidizing gas will remove more reactive carbon species forming pores and vessels and it will enhance the porous nature of activated carbon. **(Mohd Adib yahya *et al.*, 2018)**

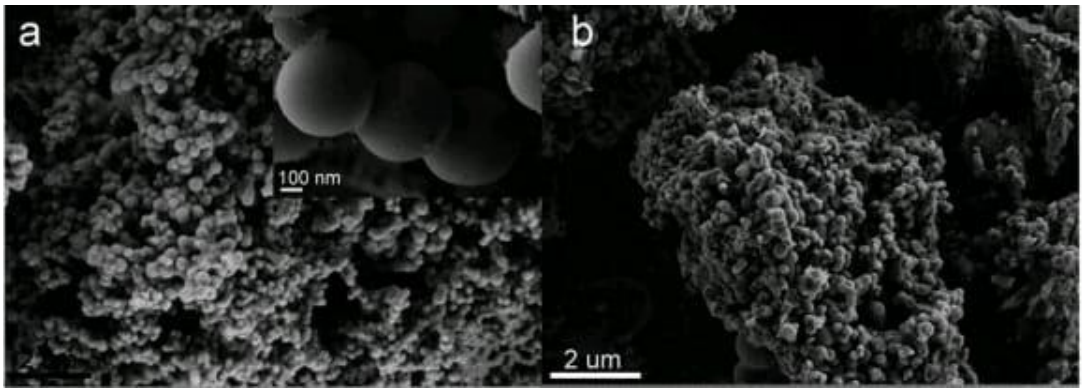


Fig: 1.4 SEM images of carbon nanosphere a) and b) porous carbon sphere with superior mesoporous structure by facile $ZnCl_2$ activation method using glucose as the carbon source. (Binbin chang *et al.*, 2014)

1.4.1 Physical Activation:

It involves two steps which is carbonization of the raw precursor in an inert atmosphere followed by activation at higher temperature ranging from 500 to 1000°C in presence of oxidizing agents such as steam, CO_2 and air that open and develop the porosity of the carbonized material.

1.4.2 Chemical Activation:

Chemical activation process involves simultaneous process of carbonization and activation by activating agents in a single step. The precursor is mixed with the chemical agent and kept for activation at higher temperature. Chemical activation requires some of the widely used chemicals such as alkali potassium hydroxide (KOH), Sodium hydroxide (NaOH), Potassium carbonate (K_2CO_3), alkali earth metal salts Zinc chloride ($ZnCl_2$) and some acids like phosphoric acid (H_3PO_4) and Sulphuric acid (H_2SO_4). These chemicals function as dehydrating agents by preventing tar formation, encouraging pyrolytic decomposition of the organic bond structure of the precursor. **(Rajashree Samantray *et al.*, 2019)**

Common ranges of activation temperature in the process of producing activated carbon with phosphoric acid, zinc chloride, potassium carbonate, sodium hydroxide and potassium hydroxide were 450-600°C, 400-900°C, 700-1000°C, 550-850°C and 450-850°C respectively. **(Zoha Heidarinejad *et al.*, 2020)**

In chemical activation with alkali, activation with KOH shows better results than NaOH in terms of surface area. KOH has been extensively used, due to its ability to produce activated carbon with a high surface area, its distribution of fine pore size under the same conditions, low environmental pollution and lower cost. **(Zoha Heidarinejad *et al.*, 2020)**

KOH reacts with char-carbon at high temperatures and releases H_2, CO and CO2 gases that are the main factors for the creation of defects and pores in carbon materials **(Alok Kumar Tripathi *et al.*, 2021)**.

In general chemical activation has more advantages than physical activation because it takes place in lower temperature and shorter time, leading to wider micropores along with higher pore volumes and higher carbon efficiency compared to physical activation.

1.4.3 Other activation methods:

Physicochemical activation:

Apart from physical and chemical activation, activation can be carried out simultaneously through physicochemical activation. In this process, two methods are used to produce activated carbons. i) Chemical treatment prior to carbonization (pre-carbonization). In these process, the precursors undergoes carbonization followed by impregnation of biochar and then thermal treatment in presence of oxidizing gas or carbonization in inert atmosphere and switching to oxidizing gas for physical activation at an elevated temperature between 650-850°C. **(Sumon Reza *et al.*, 2020)** ii) Chemical treatment subsequent to carbonization (post carbonization). In this process, the precursors undergo chemical treatment before thermal treatment and physical activation.

Microwave-assisted activation:

Microwave assisted activation is the combination of physical and/ or chemical activation which can produce higher quality activated carbon by one or two steps. **(Asmaa *et al.*, 2016)**

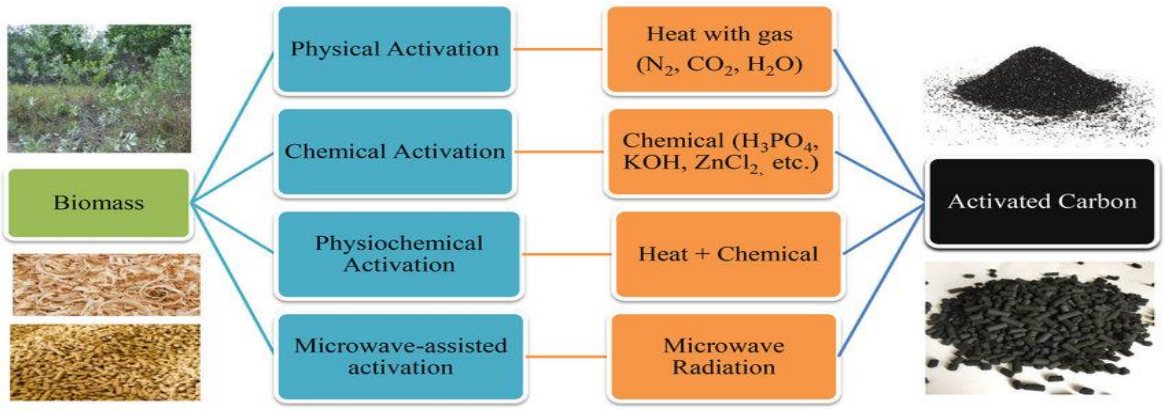


Fig: 1.5 Methods of Activation process (Sumon Reza *et al.*, 2020)

1.5 Applications of Activated carbon:

There are many applications on activated carbon including waste water treatment, water purification, industrial water treatment, CO_2 particles capturer, pharmaceutical, gold purification and electrodes for electric double layer capacitors. **(Mohd Adib Yahya *et al.*, 2018)**

1. **Metallic pollutant removal from water:**

Metallic pollutants such as heavy metals and metalloids are hazardous to water contaminants. Many studies have revealed the use of activated carbons for the low cost and easy removal of metallic pollutants. Therefore, activated carbons are widely used in purifying water containing metals like cadmium, lead, copper, iron and chromium. **(Sumon Reza *et al.*, 2020)** Cadmium is a highly toxic water contaminant, by using oil palm shell activated carbon, the cadmium is removed with a high removal efficiency of 99.5%.

2. **Adsorption of organic pollutants:**

The discharge of industrial wastes and the leaching from agricultural and forest land are the main sources of organic pollution in several water streams. The activated carbon is widely used for the removal and control of synthetic and naturally occurring organic chemicals in water. **(Mahuel Almeida *et al.*, 2007)** The most important characteristics of Activated carbon in adsorption are pore size distribution and mineral matter content.

The adsorption capacity depends on the accessibility of organic molecules to the microporosity which depends on their size. Thus, under suitable experimental conditions, small molecules such as phenol can access micropores, natural organic matter can access mesopores and bacteria can only access macropores.

3. Removal of dyes using activated carbon:

Dyes are identified to be one of the heavy pollutants of water bodies, due to the use of large amounts of colorings required in clothing, paper products, paints and plastics. **(Syieluing wong *et al.*, 2018)** Activated carbon is used to remove various dyes. For example, Methylene blue dye is removed using activated carbon derived from biowaste which is in the adsorption capacity range from17.44-476.2 mg/g.

4. Energy related applications in supercapacitors:

Activated carbons, which are perhaps the most explored class of porous carbons, have been traditionally employed as catalyst supports or adsorbents, but lately they are increasingly being used or find potential applications in the fabrication of supercapacitors. **(Marta Sevilla *et al.*, 2014)**. Activated carbon is the material used in commercial EDLCs due to its high surface area, low cost, adequate electrical conductivity, chemical stability and availability. To date, a variety of carbon materials have been used to fabricate supercapacitor electrodes (i.e mesoporous template carbons, Zeolite templated carbon, carbon xerogels, carbon nanotubes etc.,) but activated carbons are still the primary choice. **(Marta Sevilla *et al.*, 2014)**

Fig : 1.6 Various applications of activated carbon (Abm Kamrul Hasan *et al.*, 2020)

1.6 Plant description (i):

Plumeria pudica is an evergreen species of the genus plumeria (Apocynaceae) and it is a medium sized tree with profuse branching and local to Columbia, Venezuela and Panama. Plumeria is known for its exotic fragrance and its ornamental applications. The common names of this plant are wild plumeria, bridal bouquet, white frangipani, fiddle leaf plumeria, nag champa.

Picture courtesy: (https://images.app.goo.gl/CXfvhLgp9y1ZV42BA)

Fig: 1.7 *Plumeria pudica* plant

Taxonomic classification of *Plumeria pudica*

Kingdom	**Plantae**
Sub kingdom	Tracheophytes
Class	Dicotyledons
Subclass	Asterids
Order	Gentianales
Family	Apocynaceae
Genus	*Plumeria*
Species	*Pudica*
Synonyms	*Plumeria caracasana, plumeria cochleata*

Table: 1.1 Scientific classification of *Plumeria pudica* plant

1.6.1 Phytochemical constituents of *Plumeria pudica :*

Plumeria pudica plant contains some of the phytochemical constituents such as alkaloids, carbohydrates, glycosides, saponins, flavonoids, Phenolic compounds, proteins.

1.6.2 Characteristics of *Plumeria pudica* Plant:

Fig: 1.8 Characteristics of *Plumeria pudica* plant

1.6.3 Useful parts of *Plumeria pudica:*

Not only, plumeria blossoms make a fragrant attractive addition to the home or garden, they have various medicinal uses.

- Its root bark is used in the treatment of blennorrhagia, herpes and syphilis.
- The stem is used for treating ulcers, skin diseases.
- Flowers are used in a complex pectoral syrup for treating chest coughs and grips.
- In the ancient Indian healing science of Ayurveda, the oil of plumeria is considered as a warming oil and is thought to be effective in treating fear, anxiety and insomnia.

It has anti-inflammatory, antipyretic, anti-tumour, anti-microbial, diuretic, anti-allergic, anti-ulcer, and antioxidant properties. **(Gunasekaran Suriyakala *et al.*, 2021)**

1.7 Plant description (ii):

Tecoma capensis, the cape honeysuckle, is a species of flowering plant in the family Bignoniaceae, native to Southern Africa. It is an attractive ornamental garden plant commonly used for screening and decorative purposes, and can also be trimmed to form a hedge. The origin of the genus name, *Tecoma*, is a contraction of the Mexican name for one of the species, "*tecoma xochitl*". The species name, *capensis*, means "of or from the cape".

An erect, Scrambling shrub, it grows to 2-3 m in height, the leaves are up to 15 cm long. They are opposite, slightly serrated, green to dark-green and pinnate with 5 to 9 oblong leaflets. The flowers are tubular, narrow, about 7.5 cm long and are produced at different times throughout the year. *Tecoma capensis* is an evergreen plant in warm climate areas but loses its leaves in cooler areas.

The cape honeysuckle has several cultivars with flower colors ranging from yellow, apricot, orange and red.

Picture courtesy :(https://en.m.wikipedia.org/wiki/Tecoma_capensis)

Fig: 1.9 *Tecoma capensis* plant

Scientific classification of *Tecoma capensis* plant

Botanical name	***Tecoma capensis***
Synonyms	*Tecomaria capensis, Bignonia capensis*
Family	Bignoniaceae
Order	Lamiales

Kingdom	Plantae
Genus	*Tecoma*
Species	*T. capensis*

Table: 1.2 Scientific classification of *Tecoma capensis* plant

1.7.1 Phytochemical constituents of *Tecoma capensis* plant leaves:

Tecoma capensis plant leaves contain some of the phytochemical constituents such as phenols, glycosides, flavonoids, proteins, saponins and steroids.

1.7.2 Uses of *Tecoma capensis*:

- The bark is used in traditional medicine to relieve pain and sleeplessness, to bring down fevers, to treat chest ailments such as bronchitis, to treat stomach pains, diarrhea and dysentery.
- Leaves are also used to treat diarrhea and gastroenteritis.
- Dried and powdered bark is rubbed around the teeth to treat bleeding gums.
- It has antibacterial, antiviral, antioxidants in them that help heal the body naturally.

1.7.3 Characteristics of *Tecoma capensis* plant:

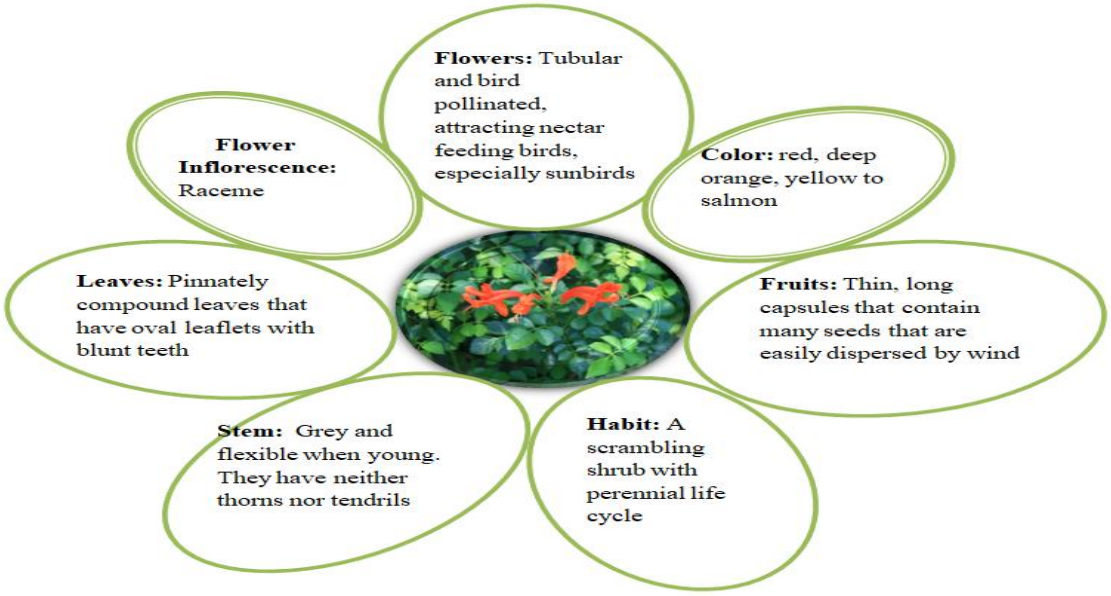


Fig: 1.10 Characteristics of *Tecoma capensis* plant

1.8 Objectives:

- To synthesize carbon using green carbon precursors by a facile and low cost carbonization method.
- To activate the as prepared carbon materials using KOH as activating agent [1:3].
- To understand the comparative study of carbon materials before and after activation.
- To characterize the as synthesized Pre-carbonized and activated carbon materials using FT-IR, XRD, UV-Visible spectroscopy, Raman spectroscopy and TGA analysis.

2. REVIEW OF LITERATURE:

Literature relevant to the present study entitled "**Microwave-assisted synthesis and characterization of biomass-derived porous carbon from natural precursors *Plumeria pudica* and *Tecoma capensis* leaves"** is reviewed and summarized in this chapter.

- A green and environmentally friendly biomass ***Hibiscus sabdariffa*** **fruit** was chosen as a green carbon precursor for preparing porous activated carbon by carbonization method at 800°C for 2h and for the activation process, KOH was used. The obtained sample were characterized by using FE-SEM, TEM, XRD, Raman spectroscopy, BET and XPS techniques. TEM images reveal the presence of highly porous nanosheets structure. These results conclude that the increasing carbonization temperature to 800°C increases the release of volatiles in the precursors and it leads to enhanced development of pores and creates new pores. **(Hamouda Adam Hamouda *et al.*, 2021)**

- A green and sustainable biomass cellulosic waste of ***Sapindus trifoliatus*** **nut shells** was chosen as a carbon precursor for preparing porous activated carbon nanofibers by carbonization at 700°C for 3h under N_2 atmosphere followed by physical activation through CO_2 purging for 2h. The prepared sample was studied using FT-IR, TGA, BET, XRD and FESEM techniques. XRD results reveal the amorphous nature containing low crystalline form and higher degree of interlayer distance. These results show that the prepared sample contains high specific surface area and large pore volume. Therefore, cellulosic biomass would be a promising precursor preparing porous activated carbon materials for high performance supercapacitors. **(Murugan Vinayagam *et al.*, 2021)**

- Flowers of ***Borassus flabellifer*** were used as a green carbon precursor for producing activated carbon by carbonization in an inert atmosphere at 400°C for 2h and activated using KOH at 650°C for 3h. The obtained sample were studied using TEM, XRD, Raman spectroscopy, FT-IR and BET techniques. The obtained sample had a pore size distribution of 1.96nm which showed excellent electrochemical performance. **(Zaharaddeen *et al.*, 2021)**

- A eco-friendly dragon fruit (***Hylocereus undatus***) **peel** was chosen as a green carbon precursor for preparing N-doped mesopore-dominated activated carbon (N-dfAC) by carbonization method followed by KOH activation and melamine as the dopant. The obtained N-dfAC was analyzed by SEM, EDX, TEM, XPS, Raman spectroscopy and BET techniques. TEM images reveal the presence of hierarchical porous activated carbon structure and the XPS confirms the presence of doped N atoms. **(Dayakar Gandla *et al.*, 2021)**

- A green biomass resource, ***Quercus persica*** **seeds** was used to prepare activated carbon by chemical activation using KOH. The prepared sample were studied using FTIR, SEM, BET and XPS techniques. The prepared sample showed high specific capacitance of 362 Fg^{-1} and it was a promising electrode for supercapacitor. **(Seyed Abbas Borghu *et al.*, 2021)**

- A facile and cost effective method for preparing porous activated carbon by physical activation method using two different green precursors such as ***Syzygium cumini*** **fruit shells** (SCFS) and ***Chrysopogon zizanioides*** **roots** (CZR) by two step synthesis such as carbonization at 700°C in N_2 atmosphere and CO_2 activation at N_2 atmosphere. The synthesized activated carbon were then characterized using Fourier transform infrared spectroscopy (FTIR), Thermo gravimetric analysis (TGA), Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Raman spectroscopy and BET. These results highlight that biomass would act as a potential precursor for synthesizing activated carbon for high performance supercapacitors. **(Murugan vinayagam *et al.*, 2020)**

- ***Eucalyptus globulus*** **seeds** (EGS) was chosen as a green carbon precursor for preparing porous activated carbon by a simple hydrothermal method and KOH as the activating agent. The prepared activated carbon was analyzed by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM),Energy dispersive X-ray analysis (EDX),X-ray photoelectron spectroscopy (XPS) and BET techniques. The result of BET reveals the EGS activated carbon prepared at 900°C showed the highest specific surface area. **(Sofia Jeniffer Rajasekaran *et al.*, 2020)**

- ***Helianthus* pallet,** a biomass byproduct waste, was chosen as a carbon precursor for preparing Template-like N,S and O tridoping activated carbon by pulverization followed by pre-carbonization and KOH etching. The characterization of the prepared sample was made through XRD, SEM, HRTEM, Raman spectroscopy and XPS techniques. These results concluded that the obtained power density and energy density can promote the biomass waste into high quality carbon material for energy storage. **(Ji yan *et al.*, 2020)**

- A low cost, environmentally friendly, renewable green precursor **Oil palm empty fruit bunches (EFB)** was used to prepare activated carbon by carbonization process at 400°C for 4h followed by chemical activation using KOH as the activating agent. To increase the capacitance nitrogen doping was done using melamine as a nitrogen source. The prepared sample was examined by FE-SEM, BET, FT-IR, XRD and XPS techniques. These results concluded that the oil palm EFB biowaste can be a valuable active electrode material for supercapacitors. **(Huyen Tran Thi Dieu *et al.*, 2020)**

- **Pinecone** biomass was chosen as a green precursor for synthesizing activated carbon by the conventional pyrolysis process and it was activated by KOH as the activation agent. The prepared sample was analyzed through FESEM, Raman spectroscopy, XPS, Nitrogen adsorption-desorption isotherm and BET techniques. These results show that the obtained activated carbon has high surface area and pore density with a considerable amount of oxygen functionalities on the surface. **(Murugesan Rajesh *et al.*, 2020)**

- A cheap, sustainable and environmentally friendly resource **Walnut shell** was chosen as a biomass precursor for synthesizing activated carbon by one step chemical activation using KOH as the activating agent. The prepared sample were characterized using SEM, XRD, XPS, FT-IR, Nitrogen adsorption-desorption and BET techniques. These results reveal that the prepared sample has large surface area and moderate porosities with excellent electrochemical performance. Therefore, high quality activated carbon can be prepared with high efficiency by using walnut shell as a biomass precursor. **(Dawei Lan *et al.*, 2020)**

- Agricultural waste, ***Allium sativum* peel** was chosen as the biomass precursor for preparing porous nano carbon by non-templating technique without any activation by

pyrolysis method. Raw sample was characterized using TGA, FESEM, EDX, HRTEM, XRD, FTIR, Raman spectroscopy and BET techniques. TEM images reveal the presence of a spherical form of synthesized porous nano carbon. These results conclude that the prepared sample contains abundant oxygen-containing functional groups which are responsible for conductive electrode and electrolyte interaction. **(Vinay S. Bhat *et al.*, 2020)**

- A facile and cost effective method was used for the preparation of nitrogen doped porous biocarbon using **Grape marcs** as a green precursor through carbonization method using urea as N-doping agent and KOH as activating agent. The obtained sample was characterized through TGA, SEM, TEM, XRD, Raman spectroscopy and XPS techniques. These results conclude that the obtained sample has large specific surface area with hierarchical porous structure and numerous N-containing groups with excellent charge storage performance. **(Jinhao zhang *et al.*, 2020)**

- Naturally available biomass waste, **American poplar fruit waste,** was chosen as a carbon precursor for preparing tubular-like porous carbon via simple carbonization method at 650°C about 2h followed by an activation process using KOH as the activation agent. The prepared sample was characterized through SEM, HR-TEM, TGA, XRD, BET Raman spectroscopy and XPS analysis. These results conclude that the obtained sample of American poplar fruit waste would be an inexpensive precursor for preparing porous carbon and also a suitable electrode candidate for supercapacitor. **(Rajesh kumar *et al.*, 2020)**

- Marine biomass ***Sargassum*** was chosen as a carbon precursor for preparing 3 dimensional porous carbon with mesoporous channels by aqueous ammonia treatment and it was activated by KOH. The prepared sample was analyzed by HRTEM, XRD, Raman spectroscopy, XPS and BET techniques. HRTEM results confirm the presence of 3 dimensional porous carbon structure with a large number of micro and mesopores. These results confirm that the seaweed biomass can be a high performance electrode material for supercapacitors. **(Xiaopeng Jia *et al.*, 2020)**

- A green and sustainable renewable biomass precursor **Jujube fruit** was used to prepare hierarchical porous carbon by two step process which includes pre-carbonization at 600° C for 2h and it was activated with NaOH at 650°C for 2h which results in the formation of highly activated hierarchical structure. The obtained sample was analyzed using some characterization techniques such as SEM, HR-TEM, EDAX, TGA, XRD and XPS analysis. All the outstanding results conclude that the prepared sample would be a commercial and promising electrode material for high performance energy storage devices. **(Viengkham yang *et al.,* 2020)**

- A low cost biomass derived porous carbon was prepared using **Soybean** activation using KOH and then carbonization. The obtained sample were characterized through BET, FESEM, Raman spectroscopy and XPS techniques. SEM images reveal the presence of rich porous network structure. These results highlight that the obtained sample has a high specific surface area with hierarchical pore structure. **(Hsiu-ying chung *et al.,* 2020)**

- ***Laminaria japonica***, one of the most abundant seaweed, was chosen as the green carbon precursor for preparing porous carbon material by a simple carbonization method and for the activation process, KOH was used as an activation agent. The obtained sample were characterized using FE-SEM, Raman spectroscopy, XRD, XPS and BET techniques. From the characterization result, it can be seen that the optimum carbonization and activation temperature at 800°C showed the highest specific surface area and total pore volume of 1.38 Cm^3g^{-1} which is 80.43% of mesoporous porosity. These results prove that the obtained sample has an amorphous structure with oxygen functional groups and promising electrode material for supercapacitor. **(Youliang cheng *et al.,* 2020)**

- Green carbon precursor ***Moringa oleifera*** **fruit shells** were used to synthesize activated carbon by carbonization method at different temperatures 600-900°C followed by $ZnCl_2$ activation. The obtained samples were characterized using SEM, EDAX, XRD and FT-IR techniques. These results concluded that the activated carbon with a carbonization temperature of 800°C has the highest capacitance and it was a promising electrode material for supercapacitors. **(Shirley palisoc *et al.,* 2020)**

- A cost effective and renewable bio-waste **Sweet corn husk** was chosen as a green carbon precursor for preparing activated carbon by a two step process which includes carbonization in an inert atmosphere at 1000° C for 1h followed by activation using KOH in two different weight ratios 1:1 and 1:4 wt ratio of carbon to KOH respectively. The prepared samples were studied using various techniques such as FESEM, TEM, XRD, Raman spectroscopy, BET and TGA. These results highlight that the increase in weight ratio of KOH to carbon during activation, does not always lead to increase in the specific surface area and it depends upon morphology and crystallinity of carbon before activation. **(Malothu Usha Rani *et al.*, 2020)**

- A green and environmentally friendly biomass ***Sorghum* stem** was chosen as a carbon precursor for preparing highly porous carbon materials by pyrolysis at 800° C for 3h and it was activated by using KOH at higher temperatures (600,800 and 900°C). The prepared samples were characterized through FE-SEM, TEM, XPS, Raman spectroscopy and BET techniques. It was observed that the carbon samples activated at higher temperatures have a high specific area. These results reveal that the *Sorghum* stem is a potential carbon precursor for supercapacitor applications. **(Minijun kim *et al.*,2020)**

- A green and eco-friendly carbonaceous precursor ***Butnea monosperma* flower pollen** was used to synthesize activated carbon using $ZnCl_2$ as the activating agent by one step thermal activation process. The obtained sample was characterized by Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Thermo gravimetric analysis (TGA), Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and Raman spectroscopy. The overall results of the experiments concluded that the prepared sample had a high specific area. **(Sultan Ahmed *et al.*, 2019)**

- A low cost activated carbon was prepared using ***Cucumis melo* fruit peel** as a green precursor by a two stage process, pre-carbonization followed by chemical activation using KOH as the activating agent. The prepared activated carbon was characterized using XRD, XPS, FE-SEM, TEM, FTIR, BET and Raman spectroscopy techniques. FTIR analysis reveals the presence of amorphous carbon with large amounts of oxygen containing functional groups. FESEM images proved that the increase in temperature

resulted in the formation of micro and mesoporous morphology and it led to increase in surface area. **(Elanthamilan Elaiyappillai *et al.*, 2019)**

- Porous activated carbon material was synthesized by using hemicelluloses extracted from **Pomelo peel** as a biomass precursor by one step chemical activation using $ZnCl_2$ as activator at a low temperature of $500^{\circ}C$. The prepared sample was characterized using SEM, TEM, XRD, XPS, Raman spectroscopy and BET techniques. These results prove that the new method of preparing porous activated carbon materials using hemicellulose is feasible and it has great potential for a wide range of high performance supercapacitor applications. **(Hualin Lin *et al.*, 2019)**

- Activated carbon was synthesized using **Tea seed shell** as a biomass carbon precursor by using KOH as an activating agent and melamine as a nitrogen dopant by carbonization method. The obtained samples were characterized by BET, XPS, Raman spectroscopy, XRD and N_2 adsorption-desorption isotherm. These results concluded that the obtained carbon material has high specific surface area and also high electrochemical performance. **(Cui Quan *et al.*, 2019)**

- An inexpensive and abundant biomass ***Coconut coir pith*** was chosen as a carbon precursor for preparing activated carbon due to its high carbon content and relatively low ash content by carbonization followed by combined physical and chemical activation method. The obtained sample was studied using TGA, Proximate analysis, BET, Raman spectroscopy, SEM, TEM, FT-IR, XRD and XPS techniques. These results concluded that the prepared sample is a suitable candidate as an electrode material for supercapacitors due to its high specific capacitance. **(Sesuk *et al.*, 2019)**

- N- doped activated carbon was prepared using ***Helianthus annuus*** **seed** as a green carbon precursor by a 3 step process which includes pre-carbonization, carbonization and chemical activation using KOH. Ammonia was used as a nitrogen source for preparing N- doped activated carbon. The prepared sample was studied using some characterization techniques such as XRD, FTIR, SEM, TEM, EDAX, XPS and BET. SEM and TEM images reveal that the presence of heteroatoms in the carbon layers increased the porous nature. XRD analysis confirms the presence of hexagonal structured carbon with

increased interlayer spacing. These results show that the prepared sample has high specific capacitance and it is a suitable electrode material for a supercapacitor device. **(Juliet Christina Mary *et al.*, 2019)**

- A green and freely available **mangosteen peel waste** was chosen as a biomass precursor for preparing porous carbon via a two step process of carbonization at 600°C for 2h and activation using NaOH as an activation agent at 700°C for 2h. The synthesized porous carbon was characterized through SEM, HR-TEM, XRD, Raman spectroscopy, BET and XPS analysis. The HR-TEM analysis confirms the presence of layered like morphology and pores structures of the sample. BET surface area reveals the presence of a very high BET surface area of 2,623 m^2g^{-1}. These results prove that the prepared sample can be a promising candidate for a high performance supercapacitor. **(Viengkham yang *et al.*, 2019)**

- A value added green and bio-based waste, **egg white** which mainly contains nitrogen and oxygen functionality was chosen as a raw material for preparing porous carbon by two step method involving carbonization and activation. The first step was carbonization and freeze drying of egg white followed by activation using KOH. The obtained sample were characterized using TEM, SEM, XRD, Raman spectroscopy and XPS techniques. These results confirm that the prepared sample has three dimensional honeycomb structure composed of interconnected micropores and mesopores which results in high specific surface area. **(Ying zhu *et al.*, 2019)**

- A low cost, renewable and sustainable biomass **willow wood (*Salix sp.*)** was chosen as a green carbon precursor for preparing activated carbon by carbonization at 600° C followed by chemical activation using KOH at 800°C. The prepared sample were studied using SEM, Raman spectroscopy and XPS techniques. These results prove that the obtained activated carbon has high surface area and high pore volume with a unique combination of micropores and mesopores with excellent electrochemical performance. **(Josphat phiri *et al.*, 2019)**

- A green and sustainable biomass precursor, ***Albizia* flowers** was used to prepare hierarchical porous carbon microrods by a simple one step pyrolysis and activation using

KOH. The prepared sample was characterized using FE-SEM, TEM, XPS, TGA, BET, Raman spectroscopy and XRD techniques.TEM image revealed the presence of a lot of micropores and mesopores. These results show that the prepared sample has a high specific area and it was a promising electrode material for energy storage devices. **(Fuming Wu *et al.*, 2019)**

- ***Saccharum bengalense*** leaves were chosen as a biomass precursor for the synthesis of activated carbon using $ZnCl_2$ as an activating agent. The prepared activated carbon was characterized with X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and Brunauer-Emmett-Teller (BET) surface area. FTIR spectra reveal the presence of oxygen containing functional groups such as carbonyl group, hydroxyl groups and carboxyl groups. The prepared sample had a high specific surface area of 2090 m^2g^{-1} and it is favorable for the performance of EDLC and has a specific capacitance value of 102.6 Fg^{-1}. These results concluded that biomass derived activated carbon can be a good precursor for preparing electrode materials for supercapacitors**. (Sangeeta Rawal *et al.*, 2018)**

- **Sunflower stalk** was chosen as a green precursor for preparing hydrochar, pyrolytic carbon and activated carbon through a simple, environmentally friendly low-temperature hydrothermal carbonization and activated using KOH as the activation agent. The resultant carbon materials was analyzed using X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and BET techniques. It reveals that the sunflower stalk biomass can be used as a precursor for preparing activated carbons with high specific surface area and high electrochemical storage capacity. **(Xiaodong wang *et al.*, 2018)**

- **Corn straw biochar** was chosen as a carbon precursor for preparing porous carbon material by flash pyrolysis using KOH as a activating agent. The samples were characterized by various techniques such as SEM, EDX, TEM, XPS, XRD, Raman spectroscopy and BET techniques. These results confirm that the obtained biochar based carbon materials have hierarchical micro-meso-macro porosity and very high specific

surface area. It reveals that the biochar based porous carbons are promising electrode materials for supercapacitors. **(Zhipeng Qiu *et al.*, 2018)**

- A renewable plant waste, **Bamboo shoots shells** was chosen as a green precursor for preparing activated carbon by using KOH and $ZnCl_2$ as activators through a one step activation method at 700° C for 2h. The KOH activated sample was represented as KAC and $ZnCl_2$ activated sample as ZAC. The resulting samples were characterized through FE-SEM, HR-TEM, BET, XPS, XRD and N_2 adsorption and desorption isotherms. The N_2 adsorption and desorption isotherm reveals that the KAC sample contains mainly micropores and few mesopores while the ZAC sample has more mesopores than micropores. These results highlight that activated porous carbon from plant waste has excellent electrochemical performance. **(Junjian Han *et al.*, 2018)**

- A green and sustainable biomass precursor **Baobab fruit shell** was used to prepare activated carbon through the carbonization process at 800°C for 3h and it was activated by using KOH and H_3PO_4. The obtained samples were analyzed by using SEM, XRD, Raman spectroscopy and XPS techniques. These results conclude that the obtained samples contains hierarchical porous carbon, in which the KOH activated sample contain honeycomb-like structure with a high specific surface area of 1059 m^2g^{-1} and H_3PO_4 activated sample contain spherical carbon with high specific surface area of 991.7 m^2g^{-1} and it was a suitable electrode material for high performance supercapacitor **(Asim A. Mohammed *et al.*, 2018)**

- Porous activated carbon was synthesized using **Rotten carrot** as a green carbon precursor by chemical activation using $ZnCl_2$. The prepared sample were studied using FESEM, TEM, XRD, Raman spectra and TGA techniques. These results conclude that the prepared carbon has high specific capacitance and it is a suitable electrode material for a supercapacitor. **(Sultan Ahmed *et al.*, 2018)**

- **Peanut shell** was chosen as a green carbon precursor for preparing hierarchical porous carbon by hydrothermal treatment, $ZnCl_2$ activation and pyrolysis. The obtained sample were characterized using XRD, SEM, Raman spectroscopy and BET technique. The prepared sample consists of micropores, mesopores and macropores structure with large

surface area with excellent capacitive electrochemical performance. **(Zuoan xiao *et al.*, 2018)**

- A green and environmentally friendly biomass precursor, ***Pueraria***, the root of Kudzu, was used to prepare nitrogen-doped porous activated carbon by two steps. Firstly, *Pueraria* powder and melamine were fully mixed and hydrothermally treated, followed by pyrolysis and activation using K_2CO_3. The prepared sample were studied using SEM, TEM, XPS and XRD techniques. The prepared sample exhibited a high BET surface area of 2321 m^2g^{-1} with 99% small size mesoporous structure and it is a promising electrode material for supercapacitors. **(Xiuli Han *et al.*, 2018)**

- A green and sustainable carbon precursor ***Cotonier strobili* fibers** was used to prepare activated carbon tubes by a KOH chemical activation method. The prepared sample were studied using SEM, TEM, XRD, BET, XPS and Raman techniques. These results confirmed that the prepared sample has high surface area and it is a promising electrode material for supercapacitors. **(Xiao-Li-Su *et al.*, 2018)**

- A sustainable biomass carbon precursor, ***Torreya grandis* shell, was** used to synthesize activated carbon by carbonization at 800°C and KOH activation. The obtained sample were analyzed using SEM, TEM, XRD, XPS and BET techniques. These results conclude that the prepared sample has high specific surface area and high specific capacitance. Therefore, this electrode material is not only low cost but also high performance in supercapacitor applications. **(Huaqing xuan *et al.*, 2017)**

- An environmentally friendly biomass precursor, **Orange peel** was used to synthesize activated carbon by a facile and economical carbonization process at 600°C followed by KOH activation. The prepared sample were studied using XRD, Raman spectra and BET techniques. These results confirm that the prepared sample has mesopores with diameter ranging from 4 to 13 nm with high specific surface area. **(Kaipannan Subramani *et al.*, 2017)**

- A cheap and environmentally friendly green carbon precursor **Loofah sponge** was used to prepare 3D porous activated carbon by carbonization at 600° C and it was activated at 800°C using KOH as the activating agent. The prepared samples were analyzed by SEM,

TEM, BET, XRD, XPS and Raman spectroscopy. These results revealed that the loofah sponge derived porous carbon material can have excellent capacitive performance due to their hierarchical porous structures and the presence of heteroatom functionalities. **(Xiao-Li su *et al.*, 2017)**

- Activated carbon was synthesized using ***Alternanthera philoxeroides***, a harmful aquatic plant as a biomass precursor by pre-carbonization at 450°C and it was activated at 800°C using KOH as the activating agent. The morphology and elemental composition of the sample were characterized by FESEM, XPS, EDS, TEM, XRD and BET techniques. This study reveals that the harmful aquatic plant can be converted into valuable carbon material with high specific surface area and abundant porosity. **(Jiangfeng Li *et al.*, 2017)**

- ***Acacia auriculiformis* tree bark** was chosen as a carbon precursor for preparing activated carbon by a facile and environmentally friendly carbonization process using KOH as the activating agent. The prepared activated carbon was characterized using Field emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM), Energy dispersive X-ray (EDAX), X-ray photoelectron spectroscopy (XPS), Thermo gravimetric analysis (TGA), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and BET techniques. It revealed that the prepared activated carbon has a high specific surface area and it is a non toxic carbon source for EDLC materials in energy storage. **(Damilola Momodu *et al.*, 2017)**

- **Tobacco rods** were chosen as a biomass precursor for the synthesis of carbon material by hydrothermal carbonization and it was activated by using KOH as the activating agent. The obtained carbon material was analyzed using XRD, Raman spectroscopy, SEM, XPS, TEM, FT-IR and BET techniques. These results concluded that the obtained carbon material has hierarchical porous structure, high specific surface area with numerous heteroatom groups and good electrical conductivity. Therefore, by using tobacco rods low cost and high performance electrode material can be prepared. **(Yong-Qing zhao *et al.*, 2016)**

- A green and environmentally friendly sustainable biomass precursor ***Aloe vera*** **leaf** was used to prepare activated carbon by carbonization method at 400°C for 3h and it was activated by using KOH and heat treated at 600, 700 and 800°C. The obtained samples were studied using XRD, FE-SEM, FT-IR,TGA, Raman spectroscopy, XPS and HR-TEM. FT-IR spectra confirms the presence of oxygen containing functional groups on their surface in all the three samples. TGA profiles of 600°C sample showed a major weight loss between 450 and 550°C due to complete decomposition at carbon in air, whereas the 700 and 800°C samples showed the complete decomposition at 550-650°C due to the formation of structurally uniform carbon atoms at higher temperature. These results conclude that the sample activated at 700°C showed best activity compared to 600 and 800°C. **(Karnan *et al.*, 2016)**

- Agricultural waste **Rice straw** (*Oryza sativa*) was chosen as a biomass precursor for preparing porous activated carbon by a two step process which includes carbonization at 600°C for 4h followed by chemical activation using KOH. The resultant sample were characterized using XRD, FT-IR, TGA, FE-SEM and HR-TEM techniques. FT-IR spectroscopy confirms the presence of various functional groups. These results prove that the activated rice straw derived carbon has a combination of meso and microporous structure that results in a large specific surface area which is a suitable electrode material for a supercapacitor. **(Sudhan Nagarajan *et al.*, 2016)**

- Mesoporous carbon was prepared from carbon spheres derived from hydrothermal carbonization of **Sucrose**, followed by KOH activation. The prepared samples were characterized by SEM, TEM, BET, XPS and Raman spectroscopy. TEM images reveal that the porosity of these carbon is made up of randomly distributed uniform mesopores and micropores with 1-5 nm in sizes. These results highlight the simple, low cost and effective method for preparation of electrode materials using biomass. **(Lu Mao *et al.*, 2015)**

- Activated carbon was prepared from the environmentally friendly biomass **Rice husks** by chemical activation using KOH. The prepared activated carbon was analyzed by Thermo gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Scanning electron microscope (SEM) and BET techniques. These results show

that it is possible to prepare activated carbons with high microporosity using small amounts of KOH, which is environmentally friendly and economical. **(Young-Jung *et al.*, 2015)**

- A low cost nitrogen-doped porous carbon was prepared using **Potato waste residue** as a carbon precursor using $ZnCl_2$ as the activating agent and melamine as a nitrogen doping agent by carbonization method. The characterization of Nitrogen-doped porous carbon was made through SEM, XRD, N_2 adsorption/desorption and Raman spectroscopy. These results revealed that the prepared sample has extraordinary porous structure and excellent electrochemical performance. **(Guofu Ma *et al.*, 2015)**

- The **Corn Cob residue**, the main byproduct in the furfural industry was chosen as a carbon precursor for preparing porous carbon by a simple and direct thermal treatment, i.e., one-step activation without pre-carbonization was conducted by directly activating Corncob residue using low cost steam activation. The obtained sample was studied using TGA, SEM, BET and FTIR techniques. These results prove that the obtained sample has high specific surface area and moderate mesoporosity with excellent electrochemical performance. **(Wen-Hui Qu *et al.*, 2015)**

- **Cow dung**, abundant biological waste, was used as a biomass carbon precursor for preparing activated carbon by partial pre-carbonization at 450° C and it was activated using KOH as the activation agent. The prepared sample was analyzed by Field emission scanning electron microscopy (FESEM), Brunauer-Emmett-Teller (BET), Density functional theory (DFT) and X-ray diffraction(XRD). These results conclude that highly porous activated carbon can be prepared easily from biological waste of cow dung. **(Dhrubajyoti Bhattacharjya *et al.*, 2014)**

- Milk-free **Coconut kernel pulp** was chosen as a biomass raw material for preparing activated carbon by carbonization at several temperatures 600, 800 and 1000°C for 3h followed by activation using KOH. The prepared samples were characterized through XRD, Raman spectroscopy, SEM and BET techniques. These results conclude that the activated carbon prepared at 600°C had a large surface area and there was a decrease in surface area when temperature increases. **(Brij kishore *et al.*, 2014)**

- Activated porous carbon was prepared using ***Paulownia tomentosa*** **flower** as a green carbon precursor by cost effective pyrolysis carbonization at 600° for 2h followed by alkali activation. The morphologies and microstructures of the sample were studied using SEM, XRD, FTIR, XPS and BET. The prepared activated carbon showed high specific surface area, versatile pore texture with the coexistence of both micropores and meso/macropores, apparently increased hydrophilicity and moderate graphitization made the prepared sample as high performance electrode material for supercapacitor. **(Jiuli chang *et al.*, 2014)**

- ***Manihot esculenta*** was chosen as a green carbon precursor for preparing activated carbon by carbonization process using Muffle furnace at around 600-800°C for 4-6 hours followed by activation using HNO_3. The prepared sample were characterized using SEM, EDX, FT-IR, TGA and Powder X-ray diffraction (PXRD). These results revealed that the prepared activated carbon has porosity of different shape and size with different functional groups such as carbon and oxygen. **(Chubaakum Pongener *et al.*, 2014)**

- ***Eichhornia crassipes*** was chosen as a biomass precursor for preparing activated carbon using KOH as the activating agent at various temperatures. The prepared sample were characterized using XRD, SEM, FTIR and Raman spectra. Based on these results, it can be concluded that the activated carbon prepared from *Eichhornia crassipes* is a suitable electrode material for electric double layer capacitors. **(Senthilkumar *et al.*, 2013)**

- A green and environmentally friendly biomass precursor ***Argania spinosa*** **seed shell** was used to prepare activated carbon using KOH. The portions of activated carbon were further superficially modified by treating with ammonium peroxydisulfate and melamine to introduce surface oxygen and nitrogen functionalities. The obtained sample were studied using BET, XPS and Nitrogen adsorption isotherms. These results confirm that the O-rich AC showed lowest capacitance and N-rich AC showed highest capacitance. **(Abdelhakim Elmouwahidi *et al.*, 2012)**

- A cost effective activated carbon was prepared using environmentally friendly biomass precursor ***Camellia oleifera*** shell (COS) using $ZnCl_2$ as activating agent at various temperatures. The synthesized COS activated carbon was characterized using Brunauer-

Emmett-Teller (BET), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). These results reveal that the activated carbon obtained at the activation temperature of 600° C shows the maximum specific capacitance and large percentage of micropore. **(Juntao Zhang *et al.*, 2012)**

- **Sugarcane bagasse** which is a byproduct of sugarcane industry was chosen as a carbon precursor for preparing activated carbon by chemical activation using $ZnCl_2$. The synthesized activated carbon was analyzed using BET adsorption isotherm and Thermal gravimetric analysis (TGA). It has been found that the thermal pyrolysis of sugarcane bagasse without $ZnCl_2$ activation does not produce well developed pore structure, but the $ZnCl_2$ activated carbons produced excellent electrochemical performance with specific capacitance of 300 Fg^{-1} . The carbon which was prepared at 750°C using $ZnCl_2$ activation showed the highest specific capacitance. **(Thomas *et al.*, 2010)**

Table: 4.1

Comparison of various biomass derived activated carbon and their FT-IR characterization

S. No	Plants	Acti-vation	FTIR		Specific surface area (m^2g^{-1})	Electrolyte	Specific capacitance (Fg^{-1})	References
			Wave no: (Cm^{-1})	Groups present				
1	*Eucalyptus globules*	KOH	3357 2121 1692 1580 1200	O-H C-H C=O C=C C-O	2388	6M KOH	150 at 1 Ag^{-1}	Sofia Jeniffer Rajasekaran *et al.,* 2020
2	*Saccharum bengalense*	$ZnCl_2$	3554 2923 2362	O-H C-H C-O	2090	1M $LiSO_4$	102 at 2 mV/S	Sangeeta Rawal *et al.,* 2018

			1627	C=C				
3	*Cucumis Melo*	KOH	3382 2921 1721 1593	O-H C-H C=O C=C	722	1M KOH	404 at 1 Ag^{-1}	Elanthamilan Elaiyappillai *et al.,* 2019
4	Walnut shell	KOH	3500-3600 1650 1380	O-H C=O C-H	1016	6M KOH	169 at 0.5 Ag^{-1}	Dawei Lan *et al.,* 2020
5	*Allium sativum*	-	3448 2921 1633 1067	O-H C-H C=C C-O	436	4M KOH	174 at 0.1 Ag^{-1}	Vinay S. Bhat *et al.,* 2020
6	Coconut coir pith	NaOH and CO_2	3300 1570 1170	-OH C-O C=C	2056	1M H_2SO_4	232 at 0.1 Ag^{-1}	Sesuk *et al.,* 2019

7	*Aloe vera*	KOH	2900 1629 3448	C-H C=O O-H	1890	1M H_2SO_4	410 at 0.5 Ag^{-1}	Karnan *et al.*,2016
8	*Moringa oleifera* Fruit shell	$ZnCl_2$	1100 1400 1650 2350 3400	C-OH C=C C=O C-H O-H	-	3M KOH	122 at 0.5 Ag^{-1}	Shirley palisoc *et al.*, 2020
9	Rice straw *(Oryza sativa)*	KOH	3448 1733 1369 1218	-OH C=O C-H C-O	~ 1007	1M H_2SO_4	156 at 0.5 Ag^{-1}	Sudhan Nagarajan *et al.*, 2016
10	*Sapindus trifoliatus* nut	CO_2	3432 2924	O-H $-CH_2$	786	6M KOH	240 at 0.2 Ag^{-1}	Murugan Vinayagam *et al.*,

	shells		1022 879	C-O Cyclic ethers				2021
11	Corncob residue	-	3400 2900 1600~1450	Hydroxy group C-H Benzene ring	1210	6M KOH	314 at 5 Mv/s	Wen-Hui Qu *et al.*, 2015
12	*Paulownia tomentosa* flower	KOH	3460 1649 1000 1380	-OH C=O C-O-C $-CH_3$	1159	1M H_2SO_4	297 at 0.2 Ag^{-1}	Jiuli chang *et al.*, 2015
13	*Borassus flabellifer*	KOH	3433 2923 1380 1740 1626	O-H $-CH_2$ C-H C=O Aromatic rings	930	1M H_2SO_4	247 at 1 Ag^{-1}	Zaharaddeen S. Iro *et al.*, 2021

			1026	C-O				
14	*Eichhomia Crassipes*	KOH	3200 1064 1224 1430 1562 871 583	Hydroxy group C-OH C-O $-CH_2$ C=O C-H Siloxane group	-	1M H_2SO_4	509	Senthilkumar *et al.*, 2013
15	*Polyalthia longifolia* seeds	KOH	3466 2926 1650 1240 671	O-H C-H COOH C-O C-C	664	1M Na_2SO_4	365 at 1 Ag^{-1}	Rajkumar Srinivasan *et al.*, 2019s

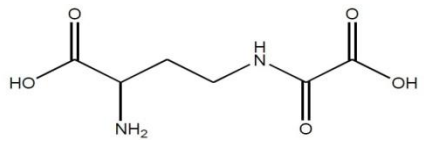
			1232	C-O-C				
16	Oil palm kernel shell	KOH	3418 2924,2848 1748 1580 1070	O-H C-H C=O C=C C-O-C	462	1M KOH	210 at 0.5 Ag^{-1}	Misnon *et al.,* 2015
17	Pinecone	KOH	3354.9 2958.9 1647.1 1100.8 559.3	O-H C-H C=O C-C -CN	1515	1M Na_2SO_4	137 at 0.5 Ag^{-1}	Abdulhakeem Bello *et al.,* 2013
18	*Sargassum wightii*	-	3445,3441 1629 1095,1084	-OH C=O Carbonyl Group	-	1M H_2SO_4	354 at 0.5 Ag^{-1}	Divya *et al.,* 2019

19	*Tremella* cell wall	KOH	3439,1478 1267,1136 901 1275 2872 2943 1589	O-H C-OH, C-O-C, C-N $=CH_2$ C=S $-CH_3$ $-CH_2$ C=C	884	2M H_2SO_4	94 at $1Ag^{-1}$	Yunqiang *et al.*, 2018
20	*Acacia auriculiformis*	KOH	1560-1650 500-1000	C=C -C-C-	1017	1M Na_2SO_4	191 at 1 Ag^{-1}	Damilola *et al.*, 2017

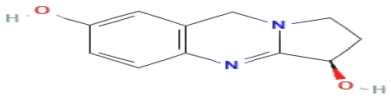
2.1 Phytochemical constituents of *Tecoma capensis* leaves:

Different extracts such as petroleum ether, n-hexane, chloroform, ethyl acetate, ethanol and water are used to study the preliminary phytochemical screening and antimicrobial activity of *Tecoma capensis* leaves. **(Ramadoss Karthikeyan *et al.*, 2015)**. The different extracts explored different phytoconstituents such as glycoside, saponin, steroids and volatile oil are present major quantities.

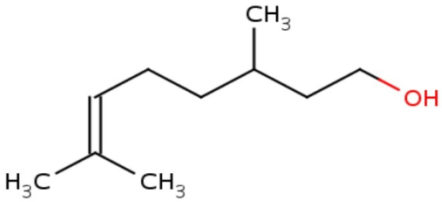
Flavonoids, proteins, tannins, carbohydrates and inulin are present in only trace amounts. The alkaloids, amino acids, lignin and waxes are absent in all the above extracts. It was found that the leaves of *Tecoma capensis* have wound healing, antihyperglycemic, anti-inflammatory, analgesic, antipyretic, anti-nociceptive and antioxidant properties. **(Ramadoss Karthikeyan *et al.*, 2015).**



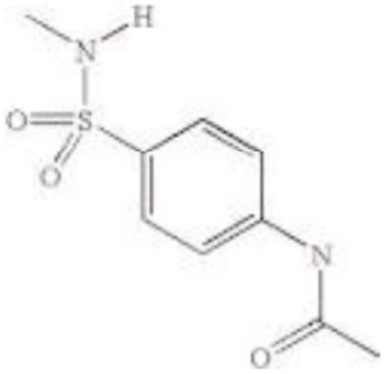
2-amino-4-[(carboxyl carbonyl)amino]butanoic acid



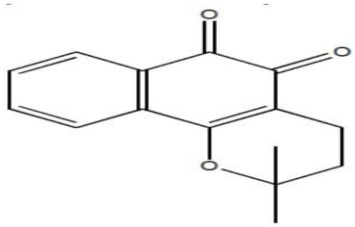
1,2,3,9- tetrahydro pyrrolo quinazoline-3,7-diol



3,7-dimethyloct-6-en-1-ol



6-hydroxy-1,3,4-oxadiazol-5-one

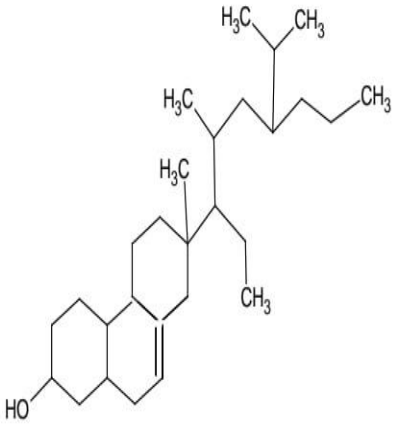


3,4-dihydro-2,2-dimethyl-2H-benzo chromene-5,6-dione

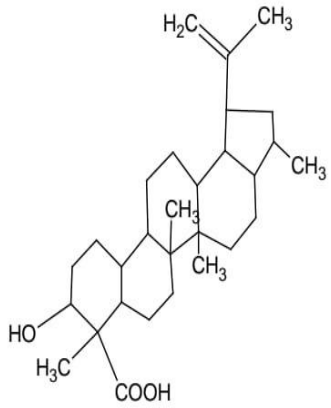
Fig.2.1 : Various phytochemical constituents in *Tecoma capensis* leaves

2.2 Phytochemical constituents of *Plumeria pudica* leaves:

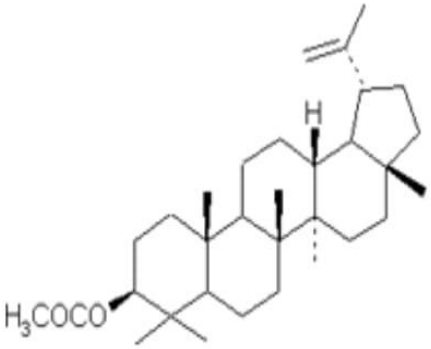
The different extracts of *Plumeria* species were analyzed for the presence of alkaloids, glycosides, terpenoids, reducing sugar, saponins, tannins, carbonyls, flavonoids and steroid. **(Devprakash *et al.*, 2015)**. It has anti-inflammatory, antipyretic, anti-tumour, antimicrobial, diuretic, cytotoxic, anti-allergic, anti-ulcer and antioxidant properties. **(Gunasekaran Suriyakala *et al.*, 2021)**



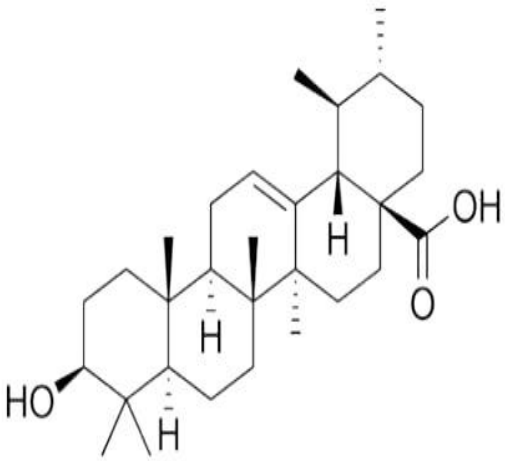
Stigmast-7-enol



Lupeol carboxylic acid



Lupeol acetate



Ursolic acid

Fig. 2.2: Various phytochemical constituents in *Plumeria pudica* leaves

3. MATERIALS AND METHODS

The methodology pertaining to the title **"Microwave-assisted synthesis and characterization of biomass-derived porous carbon from natural precursors *Plumeria pudica* and *Tecoma capensis* leaves"** is presented in this chapter.

Activated carbon were synthesized through two steps

- First step is pre-carbonization of the collected dried leaves
- Second step is the Microwave-assisted activation process using KOH as an activating agent.

3.1 Materials:

Leaves of *Plumeria pudica* and *Tecoma capensis* were collected from a garden located at Avinashilingam university, Coimbatore, Tamilnadu, India. The identification of the leaves was confirmed by the taxonomist of the Botany department of Our University.

3.2 Chemicals:

Concentrated hydrochloric acid with 1.18 specific gravity, Potassium hydroxide (KOH) was procured from Sigma-Aldrich.

3.3 Preparation of Microporous carbon:

The collected leaves of *Plumeria pudica* and *Tecoma capensis* were firstly washed with distilled water and dried at 80°C for 12 h. The dried plant samples were ground into pieces and Pre-carbonized at 300°C for 2 h in Muffle furnace to obtain the as-prepared char. Then the char was soaked in 6.0 M KOH solution in the ratio of 1:3 to obtain the KOH/char composite.

The KOH/char composite was transferred into a ceramic crucible and placed in the microwave oven to undergo a microwave treatment for 3 min at power of 600 W. After microwave treatment, the obtained sample was washed with 1.0 M HCl solution and then thoroughly washed with deionized water.

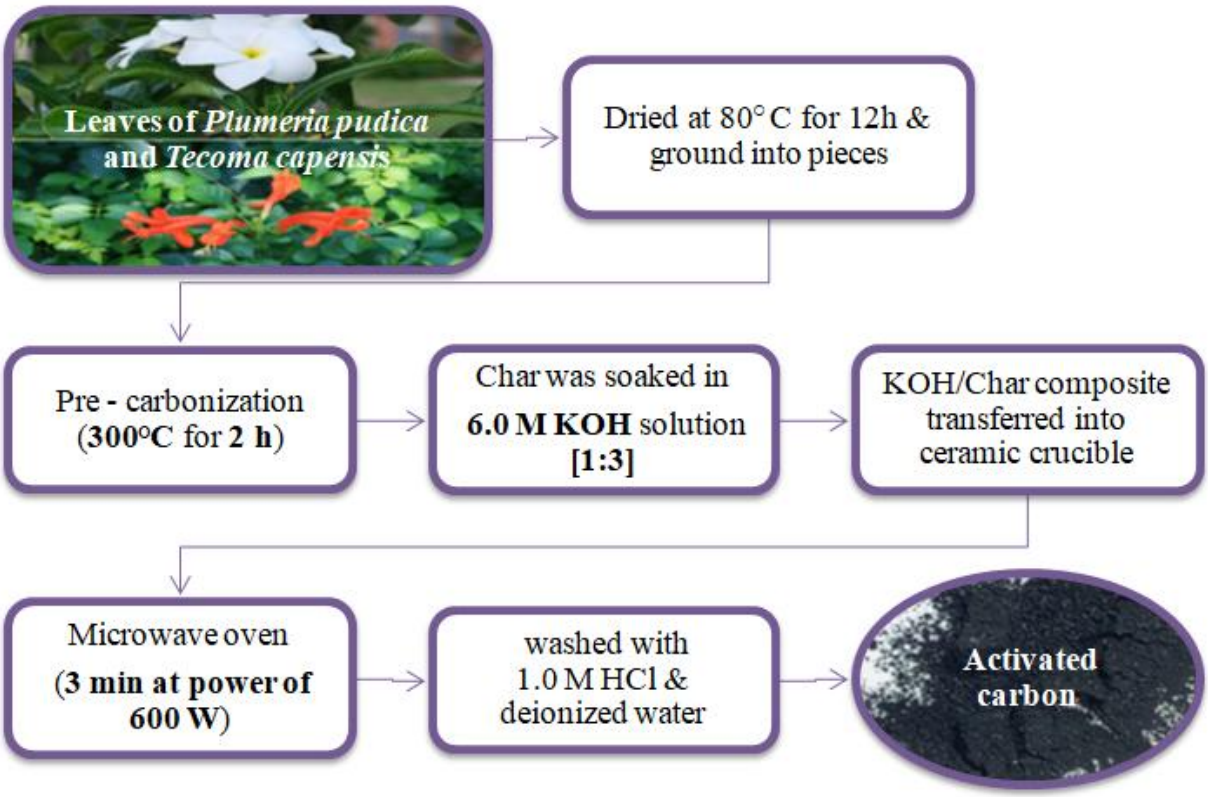


Fig.3.1: Synthesis of Activated carbon using leaves of *Plumeria pudica* and *Tecoma capensis*

3.4 Preparation of the plant extract:

Fresh leaves of *Plumeria pudica* and *Tecoma capensis* were thoroughly cleaned with water to remove debris and other contaminants, followed by distilled water and air dried at room temperature. Leaves were finely chopped into small pieces. The aqueous extract of samples was prepared by boiling the freshly collected cut leaves (10g), with 100 ml of distilled water, at 60° C for about 20 minutes, until the color of the aqueous solution changes from watery to light brown. Then the extracts were cooled to room temperature and filtered using whatman filter paper. The extracts were stored in a refrigerator in order to be used for further experiments.

a) Washing of leaves b) Drying c) Refluxing d) *Plumeria pudica* extract

Fig. 3.2: Preparation of leaves extracts a, b, c and d

3.5 Phytochemical screening of extracts

Phytochemical examinations were carried out for the extracts as per standard methods. **(Prashant Tiwari *et al.*, 2011)**

1. Detection of alkaloids: Extracts were dissolved individually in distilled water and filtered.

Mayer's Test: Filtrates were treated with Mayer's reagent (Potassium Mercuric Iodide).

Formation of a yellow coloured precipitate indicates the presence of alkaloids.

Wagner's Test: Filtrates were treated with Wagner's reagent (Iodine in potassium Iodide). Formation of brown/reddish precipitate indicates the presence of alkaloids.

Dragendroff's Test: Filtrates were treated with Dragendroff's reagent (solution of Potassium Bismuth Iodide). Formation of red precipitate indicates the presence of alkaloids.

Hager's Test: Filtrates were treated with Hager's reagent (saturated picric acid solution). Presence of alkaloids confirmed by the formation of yellow coloured precipitate.

2. Detection of carbohydrates: Extracts were dissolved individually in 5 ml distilled water and filtered. The filtrates were used to test for the presence of carbohydrates

Molisch's Test: Filtrates were treated with 2 drops of alcoholic 1-naphthol solution in a test tube. Formation of the violet ring at the junction indicates the presence of Carbohydrates.

Benedict's Test: Filtrates were treated with Benedict's reagent and heated gently. Orange red precipitate indicates the presence of reducing sugars.

Fehling's Test: Filtrates were hydrolysed with dil. HCl, neutralized with alkali and heated with Fehling's A & B solutions. Formation of red precipitate indicates the presence of reducing sugars.

3. Detection of glycosides: Extracts were hydrolysed with dil. HCl, and then subjected to a test for glycosides.

Modified Borntrager's Test: Extracts were treated with Ferric Chloride solution and immersed in boiling water for about 5 minutes. The mixture was cooled and extracted with equal volumes of benzene. The benzene layer was separated and treated with ammonia solution. Formation of rose-pink color in the ammoniacal layer indicates the presence of anthranol glycosides.

Legal's Test: Extracts were treated with sodium nitroprusside in pyridine and sodium hydroxide. Formation of pink to blood red color indicates the presence of cardiac glycosides.

4. Detection of saponins

Froth Test: Extracts were diluted with distilled water to 20ml and this was shaken in a graduated cylinder for 15 minutes. Formation of a 1 cm layer of foam indicates the presence of saponins.

Foam Test: 0.5 gm of extract was shaken with 2 ml of water. If foam produced persists for ten minutes it indicates the presence of saponins.

5. Detection of flavonoids

Alkaline Reagent Test: Extracts were treated with few drops of sodium hydroxide solution. Formation of intense yellow color, which becomes colorless in addition to dilute acid, indicates the presence of flavonoids.

Lead acetate Test: Extracts were treated with few drops of lead acetate solution. Formation of yellow color precipitate indicates the presence of flavonoids.

6. Detection of phenols

Ferric Chloride Test: Extracts were treated with 3-4 drops of ferric chloride solution. Formation of bluish black color indicates the presence of phenols.

7. Detection of proteins and amino acids

Xanthoproteic Test: The extracts were treated with few drops of conc. Nitric acid. Formation of yellow color indicates the presence of proteins.

Ninhydrin Test: To the extract, 0.25% w/v Ninhydrin reagent was added and boiled for a few minutes. Formation of blue color indicates the presence of amino acid.

8. Detection of phytosterols

Salkowski's Test: Extracts were treated with chloroform and filtered. The filtrates were treated with few drops of Conc. Sulphuric acid, shaken and allowed to stand. Appearance of golden yellow color indicates the presence of triterpenes.

9. Detection of diterpenes

Copper acetate test: Extracts were dissolved in water and treated with 3-4 drops of copper acetate solution. Formation of emerald green color indicates the presence of diterpenes.

10. Detection of tannins

Gelatin test: To the extract, 1% gelatin solution containing sodium chloride was added. Formation of white precipitate indicates the presence of tannins.

3.6 Characterization of PCC and AC:

The PCC and AC of PPL and TCL were characterized by the following studies.

UV Spectroscopy:

PC based double beam spectrometer 2202 was used to study the PCC and AC for PPL and TCL. Quartz cuvette was used and ethanol was used as the reference solvent. Stock solution for UV measurement was prepared by sonicating 5mg of PCC and AC of PPL and TCL in 10ml of ethyl alcohol. The range was set up between 200-800 nm.

Thermogravimetric analysis and Differential thermal analysis:

Perkin-Elmer Thermo gravimetric analyser is used for TGA analysis, it is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature or as a function of time with constant temperature. It is a temperature based study**.**

Thermal stability of the prepared PCC and AC of both PPL and TCL was studied by Thermogravimetric analysis. The decomposition pattern, loss of water, of the PCC and AC was determined.

FT-IR analysis:

Perkin Elmer FT-IR spectrophotometer with the **SOFTWARE – OPUS version 6.5** was used for the FT-IR analysis, to identify the presence of surface functional groups in the PPL and TCL activated and pre-carbonized samples. The spectral data of the samples were recorded in the wave number range from 4000 cm^{-1} to 400 cm^{-1}.

X-Ray diffraction analysis:

X-Ray diffraction analysis is used to analyze the nature of carbon materials and the degree of order or periodicity in the arrangement of atoms. **X-PERT-PRO Pan analytical diffractometer using Cu-Kalpha** (λ= 1.5406 nm) as an X-ray source at a generator voltage of 45 KV and current of 30 mA.

From the XRD data, the interlayer spacing of PCC and AC of PPL and TCL were calculated using Bragg's law as follows;

$$d = \lambda / 2\sin\Theta$$

From the XRD data we can also calculate the size of particles using Scherrer formula as follows:

$$D_P = (0.94 \times \lambda) / (\beta \times \cos\Theta)$$

Where, D_P =Average Crystallite size

β = Line broadening in radians

Θ =Bragg's angle

λ= X-ray wavelength.

Raman spectroscopy:

Raman spectroscopy is used to determine the structure and defects as well as the disordered nature of carbon materials.

4. RESULTS AND DISCUSSION

The present investigation entitled "**Microwave-assisted synthesis and characterization of biomass-derived porous carbon from natural precursors *Plumeria pudica* and *Tecoma capensis* leaves"** deals with the synthesis of pre-carbonized and activated carbon materials from green carbon precursors *Plumeria pudica* and *Tecoma capensis* leaves using KOH as the activating agent.

To reduce the energy consumption, pre-carbonization was done in the Muffle furnace (300°C for 2h) followed by microwave assisted activation (3 min at power of 600 W).

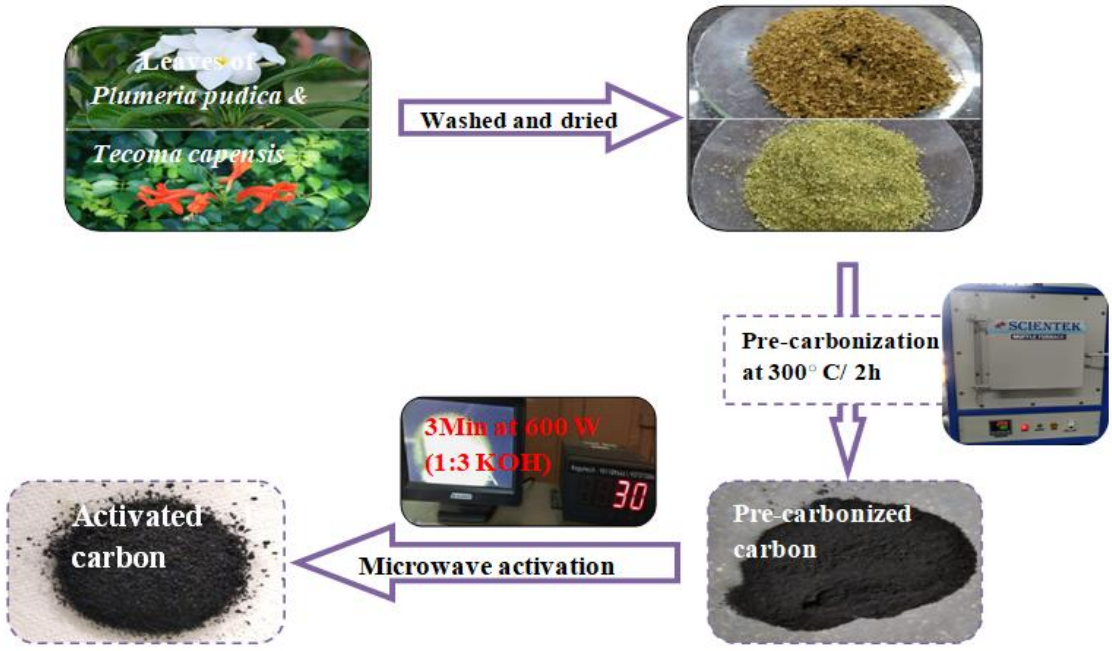


Fig: 4.1 Systematic representation of Pre-carbonized and Activated carbon synthesis

We have chosen KOH as an activating agent, as literature reflects that it induces well defined pore size distribution at lower activation temperature and high yields of carbon material. Since, KOH reacts with char-carbon at high temperatures and releases H_2, CO and CO_2 gasses that are the main factors for the creation of defects and pores in carbon materials**. (Alok Kumar Tripathi *et al.*, 2021)**

Therefore, KOH activation method is the most effective activation method due to its high carbon yield. Generally, the reaction mechanism may be as follows **(Guijun Yang *et al.*, 2018).**

$$4KOH + C \rightarrow K_2CO_3 + K_2O + 2H_2$$

Here, considering the decomposition of potassium hydroxide and the reduction of carbon, the following reactions are given.

$$2KOH \rightarrow K_2O + H_2O$$

$$H_2O + C \rightarrow CO + H_2$$

$$H_2O + CO \rightarrow CO_2 + H_2$$

$$K_2O + CO_2 \rightarrow K_2CO_3$$

$$K_2O + H_2 \rightarrow 2K + H_2O$$

$$K_2O + C \rightarrow 2K + CO$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO$$

A large amount of gas is produced in the reaction process, which is helpful to the formation of pores and easy transport of ions in an electrode of a supercapacitor. **(Guijun Yang *et al.,* 2018).**

We have chosen 1:3 ratio because, the porous carbon activated with more KOH forms larger cavities than those prepared with less KOH, showing that more carbon structures were burned off during the activation process with more activating agent. **(Manman Xu *et al.,* 2013)** Characterization studies were carried out with the synthesized pre-carbonized and activated carbons to determine their structural, pore structure and morphology.

4.1 Qualitative phytochemical analysis

Phytochemical analysis of the plant extracts of *Plumeria pudica* and *Tecoma capensis* leaves were shown table 4.1. The analysis revealed the presence of various phytochemical constituents because plants are natural chemicals. The result ++ sign indicates that highly positive, + indicates positive and – sign indicates the absence of compounds.

S.No	Phytoconstituents	Results	
		Plumeria pudica	***Tecoma capensis***
1.	Alkaloids	+	-
2.	Carbohydrates	++	-
3.	Phenols	++	++
4.	Saponins	+	+
5.	Phytosterols	-	-
6.	Amino acid	-	-
7.	Flavonoids	++	++
8.	Glycoside	-	-
9.	Proteins	+	+
10.	Tannins	-	-

Table 4.1: Phytochemical constituents of *Plumeria pudica* and *Tecoma capensis* aqueous leaf extracts

Preliminary phytochemical screening revealed the presence of alkaloids, carbohydrates, phenols, saponins, flavonoids, proteins in PPL **(Subba Rao Chamakui *et al., 2020)*** and TCL contains some of the phytoconstituents such as phenols, saponins, flavonoids and proteins **(Elamaran Tamiljothi *et al.,* 2011)**.

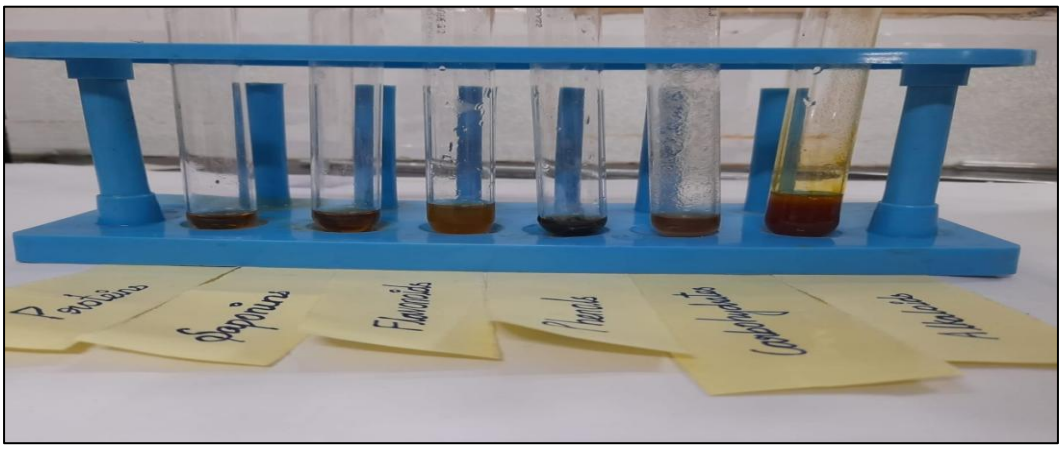


Fig: 4.2 Phytochemical analysis of *Plumeria pudica* leaves

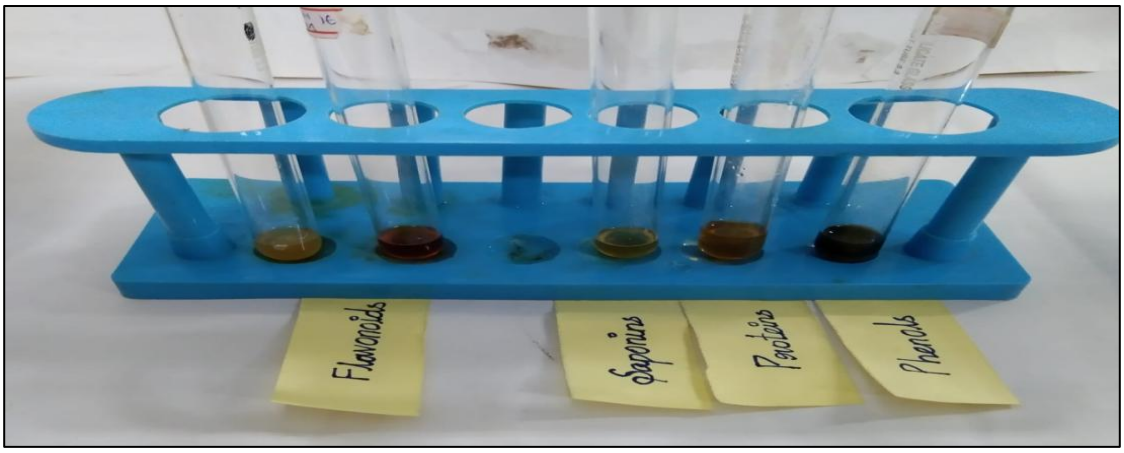


Fig: 4.3 Phytochemical analysis of *Tecoma capensis* leaves

4.2 Characterization

The obtained pre-carbonized and activated carbon of PPL and TCL were characterized and the characterization results were discussed as follows,

- Optical characterization
  - UV –Visible Spectroscopy analysis
- Surface characterization
  - FT-IR analysis
  - Raman Spectroscopy analysis
  - XRD analysis
- Thermal characterization
  - TGA analysis
  - DTA analysis

4.2.1 UV-Visible spectroscopy:

The absorption spectra of the as-synthesized pre-carbonized and activated carbons of both PPL and TCL were recorded after sonicating in ethanol using a double beam UV-Visible spectrophotometer. The UV absorption peak in carbon materials was related to electronic transitions between the bonding and antibonding π orbitals. π-π* transitions appear in the range of 180-260 nm for carbon materials. **(Sathish kumar *et al.*, 2012)**

a) UV spectrum of PC and AC-TCL:

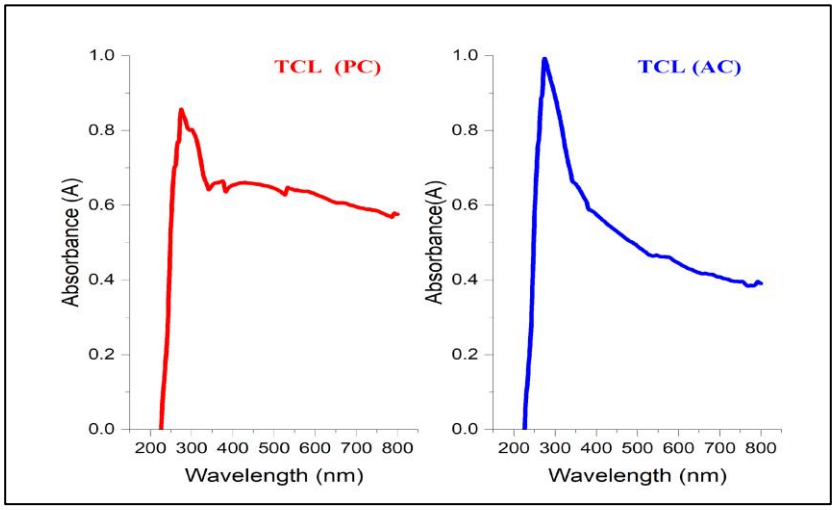


Fig:4.4 UV spectrum of PC and AC-TCL

From Fig. 4.4, the characteristic absorption peak for PC-TCL was observed at 260 nm due to the electronic transitions between the bonding and antibonding π orbitals (π-π* transition) **(Gopal Krishna Gupta *et al.*, 2021)** whereas in the AC-TCL, maximum absorption was seen in 280 nm, it is due to enhanced π-π* transition.

b) UV spectrum of PC and AC-PPL:

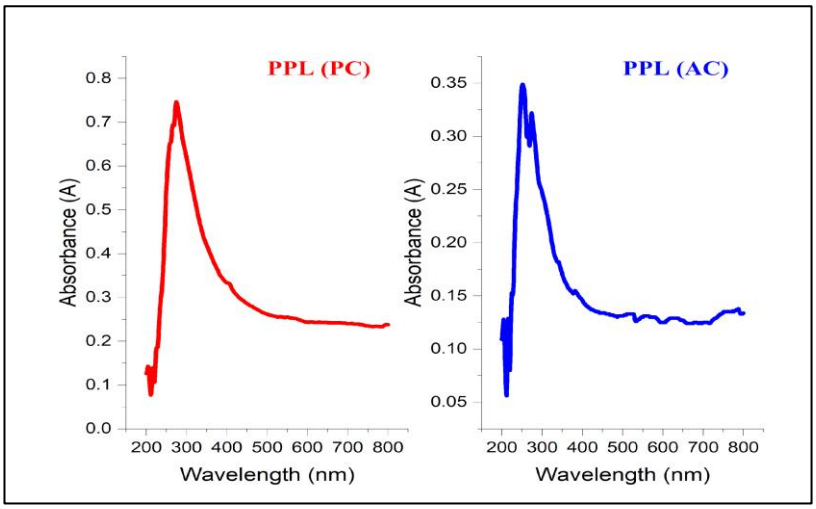


Fig: 4.5 UV Spectrum of PC and AC-PPL

From Fig.4.5, the characteristic absorption peak for PC-PPL was seen at 290 nm may be due to enhanced π-π*transition whereas in the AC-PPL, maximum absorption was seen in 250 nm due π-π* transition of carbon materials.

4.2.2 Band-gap calculation:

The energy gap for carbon materials was calculated using the formula

$$E = hc/\lambda$$

Where, h = 6.626 x 10^{-34} Joules sec (Planck's constant)

C = 2.99 x 10^{8} m/s (Velocity of light)

λ is the wavelength (Absorption peak value)

Carbon materials	Absorbance wavelength of PCC (nm)	Band gap of PCC (eV)	Absorbance wavelength of AC (nm)	Bang gap of AC (eV)
TCL	260	4.77	280	4.43
PPL	290	4.28	250	4.96

Table 4.2: Energy gap of carbon materials

From Table 4.2, it was seen that the energy gap of AC-TCL was less compared to PC-TCL suggesting that there will be easy transport of ions and it enhances the supercapacitor performance.

4.2.3 FT-IR analysis:

Surface chemical properties of synthesized pre-carbonized and activated carbon materials had been analyzed using Fourier-transform infrared Spectroscopy.

a) FT-IR of PC and AC-TCL:

The evolution of chemical composition of the PC and AC-TCL were characterized by FT-IR analysis.

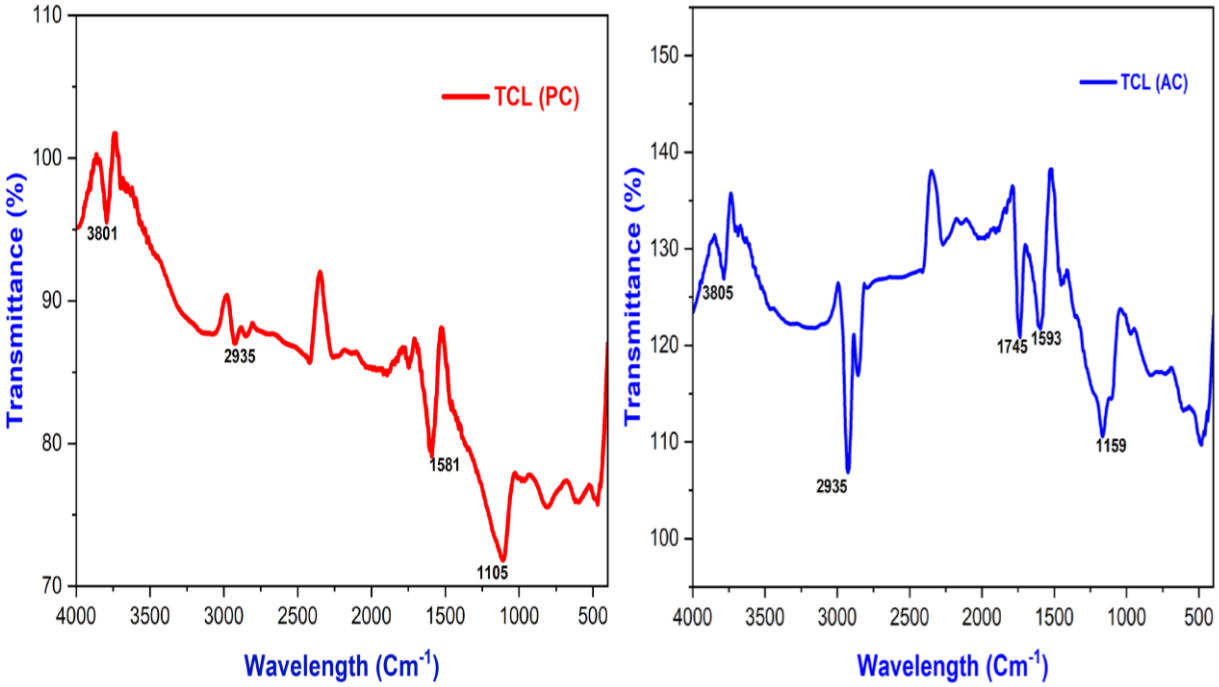


Fig: 4.6 FTIR of PC and AC-TCL

From the FTIR results shown in fig.4.6, the peak observed at 1105 cm^{-1} may be due to the presence of C-H stretching vibration. The existence of N-containing bonds was confirmed by the peak around 1581 cm^{-1}. Additionally, the peak around 3801 cm^{-1} can be assigned to the –OH stretching vibration of polyphenols or hydroxyl group whereas in the AC-TCL, the peak at 1159 cm^{-1} indicated the presence of O-H bending vibration of alcohols and furthermore, the peaks at 1593, 3805 cm^{-1} may be due to the presence of C-H stretching and –OH stretching vibration

probably due to the presence of largest percentage of phenolic –OH or alkyl hydroxyl group and also an additional small shoulder peak was also observed in 1745 cm^{-1}which may be due to the presence of C=O stretching of ester which is electrochemically more active. **(Juliet Christina Mary *et al.*, 2019)**

From the FT-IR analysis, presence of O- and N- functionality was confirmed and the nitrogen acted as a self dopant and it further enhance the capacitive behavior of the supercapacitor.

PC-TCL		AC-TCL	
Frequency (Cm^{-1})	Assignment	Frequency (Cm^{-1})	Assignment
1105	C-O stretching	1159	O-H bending
1581	N-H stretching	1593	N-H bending
2935	C-H stretching	1745	C=O stretching
3801	-OH stretching	2935	C-H stretching
-	-	3805	-OH stretching

Table 4.3: FT-IR analysis of PC and AC-TCL

b) FT-IR of PC and AC-PPL:

The evolution of chemical composition of the PC and AC-TCL were characterized by FT-IR analysis.

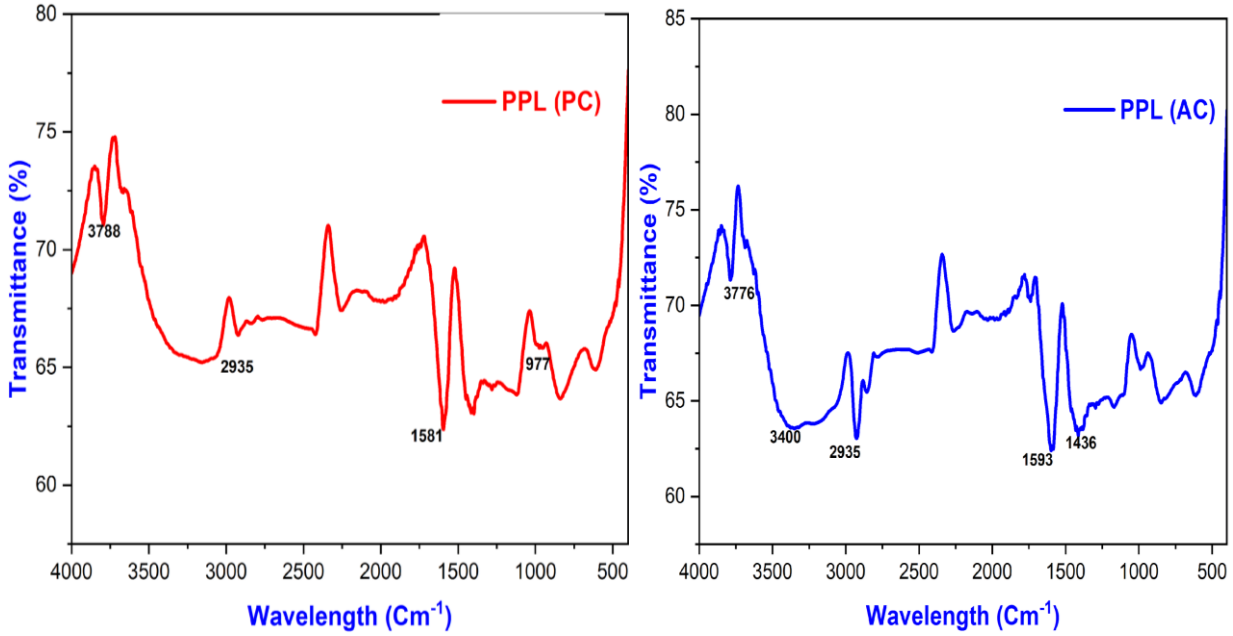


Fig: 4.7 FTIR of PC and AC-PPL

From the results shown in Fig. 4.7, the bending vibration of C=C was observed at 977 cm^{-1} and the peak observed at 1581 cm^{-1} is a characteristic of N-H bending vibration of amine group and furthermore, the peaks at 2935 and 3788 cm^{-1} may be due to the C-H stretching and –OH stretching of polyphenols /water whereas in the AC-PPL, the peak at 1436 indicated the O-H bending vibration and the peaks at 1593, 3400 cm^{-1} can be assigned to N-H bending and stretching vibration. Furthermore, the peak at 3776 cm^{-1} can be assigned to –OH stretching vibration of polyphenols/water. From the graph, it was clearly seen that after PC-PPL was activated in the microwave oven the bands corresponding to the C-H stretching vibration at 2935 cm^{-1} remained the same **(Hwei-Jay chu *et al.*, 2016)**.

FT-IR analysis confirms the presence of oxygen and nitrogen functionality. Actually, these O- and N- containing functional groups can make effects on the electrochemical capacitive behaviors **(Xu Zhang *et al.*, 2015)**.

PC-PPL		**AC-PPL**	
Frequency (Cm^{-1})	Assignment	Frequency (Cm^{-1})	Assignment
977	C=C bending	1436	O-H bending
1581	N-H bending	1593	N-H bending
2935	C-H stretching	2935	C-H stretching
3788	-OH stretching	3400	N-H stretching
-	-	3776	-OH stretching

Table 4.4: FT-IR analysis of PC and AC-PPL

4.2.4 Raman Spectroscopy analysis:

The graphitization degrees of the biomass derived carbon materials were studied using Raman Spectroscopy. It consists of two characteristic Raman peaks, D and G-band, in general the D-band was associated with defects of the carbon material whereas G-band arises due to the stretching of sp^2 carbon atoms. The D to G-band integrated intensity ratio (I_D/I_G) reflects the degree of the structural ordering with respect to graphitization and crystallinity of carbon materials. **(Hsiu-Ying Chung *et al.*, 2020)**. The lower values of I_D/I_G ratio indicated the higher graphitization degree.

The ratio I_D/I_G was inversely related to the in-plane crystallite size L_a, which can be determined using the Tuinstra-Koenig relationship

$$L_a\ (nm) = (2.4 \times 10^{-10})\ \lambda^4\ (I_D/I_G)^{-1}$$

Where λ= 532 nm which is the Raman excitation wavelength

The values of L_a are corresponding to the inter defect distance on the surface of the carbon materials.

a) Raman spectroscopy of PC and AC-PPL:

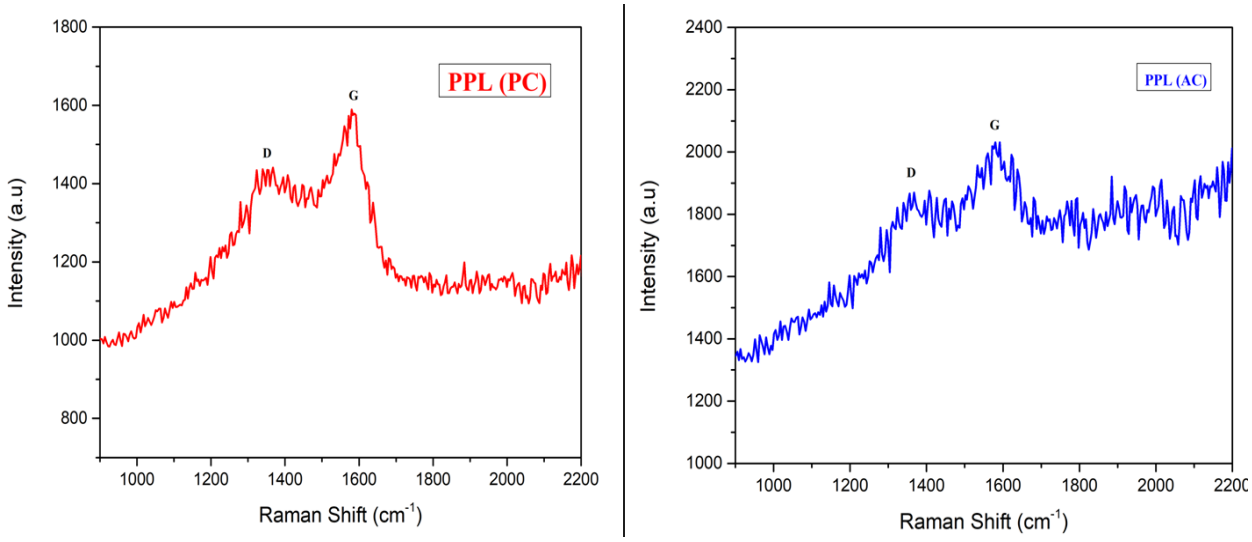


Fig: 4.8 Raman spectra of PC and AC- PPL

Raman spectra of the PC and KOH AC-PPL were shown in fig.4.8,it was identified that in PC-PPL, two characteristic Raman peaks were observed distinctly at about 1351cm^{-1} (D-band) and 1582 cm^{-1}(G-band). The D to G-band integrated ratio (I_D/I_G) was 0.91 whereas in the AC-PPL, two characteristic Raman peaks are 1359 cm^{-1} (D-band) and 1582 cm^{-1}(G-band) with the I_D/I_G ratio of 0.94. It has been seen that AC-PPL has higher I_D/I_G value than PC-PPL which indicates that KOH activation leads to lower the graphitization degree and tuning of pore size due to activation.

b) Raman spectroscopy of PC and AC-TCL:

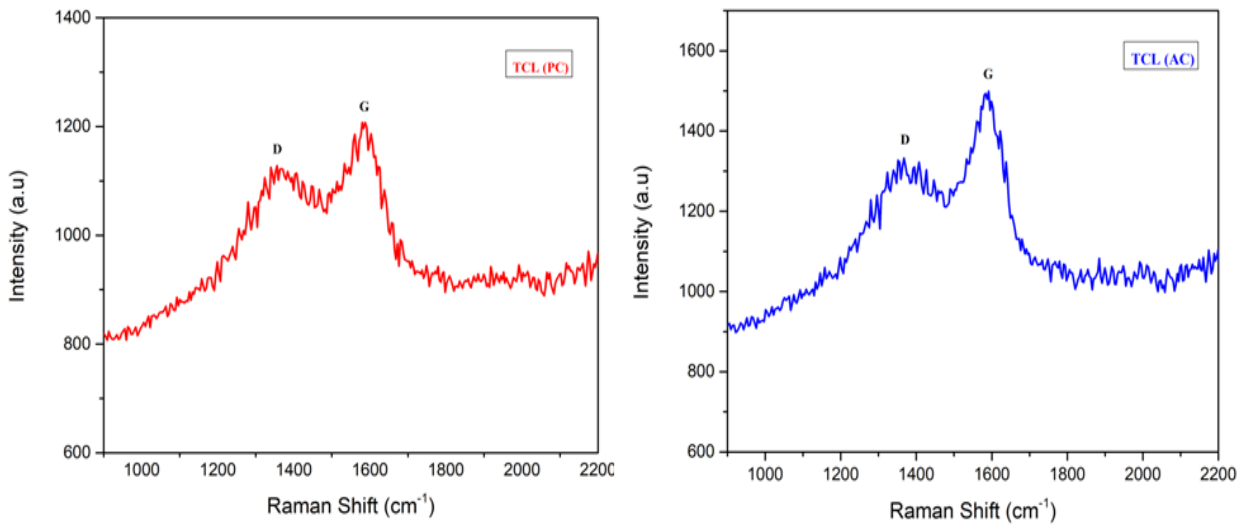


Fig: 4.9 Raman spectra of PC and AC-TCL

Raman spectra of the PC and KOH AC-TCL were shown in Fig.4.9, it was identified that in PC-TCL, two characteristic Raman peaks were observed distinctly at about 1348 cm^{-1} (D-band) and 1582 cm^{-1}(G-band). The D to G-band integrated ratio (I_D/I_G) was 0.94 whereas in the AC-TCL, two characteristic Raman peaks at 1370 cm^{-1}(D-band) and 1587 cm^{-1}(G-band) with the I_D/I_G ratio of 0.89. It has been seen that, after KOH activation the I_D/I_G value reduced from 0.94 to 0.89, which confirmed the reorientation of the defective sites and enhancement of the sp^2 hybridized carbon structures during the activation process. **(Ceran Karaman *et al.*, 2021)**

Materials	D band	G band	D band intensity	G band intensity	I_D/I_G ratio	Crystalline size (L_a) nm
PC-PPL	1351	1582	1443	1591	0.91	18.41
AC-PPL	1359	1582	1897	2020	0.94	17.82
PC-TCL	1348	1582	1129	1202	0.94	17.82
AC-TCL	1370	1587	1328	1496	0.89	18.82

Table 4.5: Parameters estimated from Raman spectroscopy for different carbon materials

4.2.5 XRD analysis:

XRD gives information about crystallinity, average crystal size and interlayer distance of the carbon materials **(Nithin Joseph Panicker *et al.*, 2021)**. To analyze the graphitization of as-synthesized pre-carbonized and activated carbon materials, the XRD technique was adopted.

a) XRD of PC and AC-PPL:

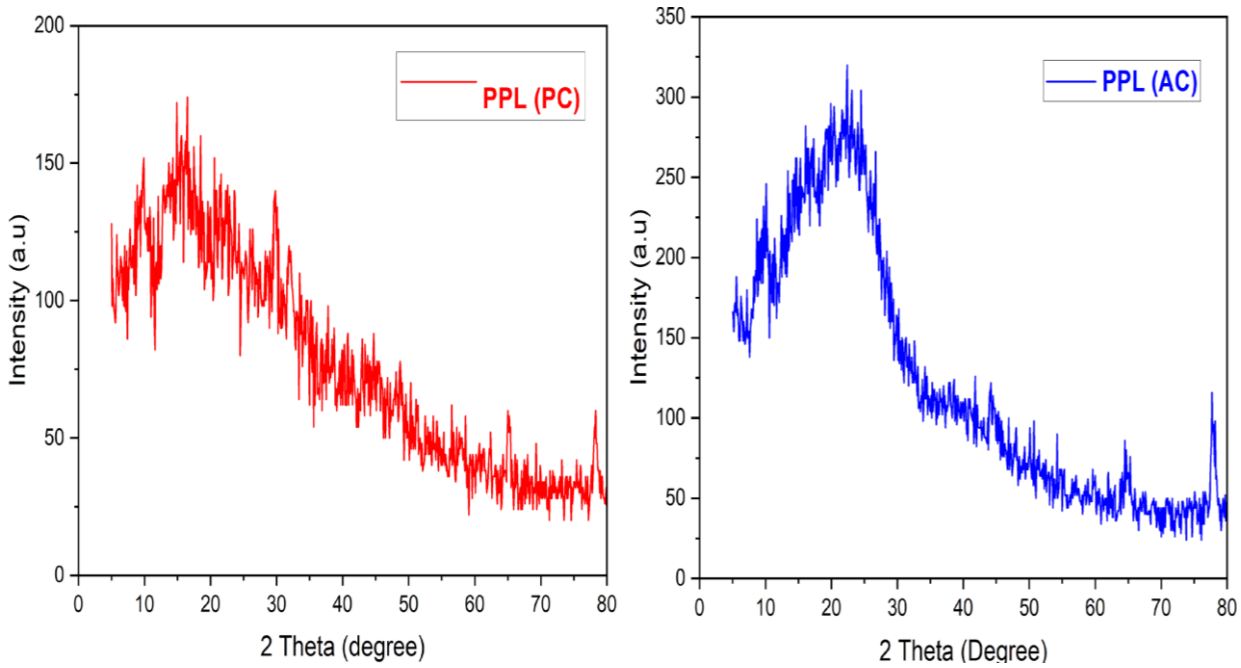


Fig: 4.10 XRD values obtained in PC and AC-PPL

XRD diffraction patterns of PC and AC-PPL were shown in Fig.4.10, Diffraction patterns of PC-PPL was seen in 2Θ= 22.5° and 29.7°. A peak at 22.5°, which can be attributed to the (002) diffraction peak of the amorphous nature of the carbon with low graphitization degree **(Dandan Shan *et al.*, 2016)** whereas in the AC-PPL, additionally peak at 77.7 A° was observed with a d spacing of 1.22 A° with a crystalline size of 14.95 nm corresponding to (110) plane. It was found that, after KOH activation there was enhanced crystalline size and it will enhance the conductivity of activated carbon material **(Sofia Jeniffer Rajasekaran *et al.*, 2020).**

From the XRD data we can easily calculate the size of particles using Scherrer formula as follows:

$$D_P = (0.94 \times \lambda) / (\beta \times \text{Cos}\Theta)$$

Where, D_P =Average Crystallite size

β = Line broadening in radians

Θ =Bragg's angle

λ= X-ray wavelength

Carbon materials	Position (2Θ)	FWHM(2Θ)	d-Spacing (A°)	Crystallite size (nm)
PC-PPL	29.7583	0.71670	2.99983	11.98
AC-PPL	77.7932	0.71360	1.22675	14.95

Table 4.6: Crystalline size of PC and AC-PPL

FWHM was a peak Full Width at Half Maximum. The crystallite or grain size was calculated using Scherrer equation. The wavelength of X-ray diffraction was 0.15418 (Cu K-alpha) was used. From the table 4.6, the crystalline size of PC and AC-PPL were found to be 11.98 and 14.95 nm.

b) XRD OF PC and AC-TCL:

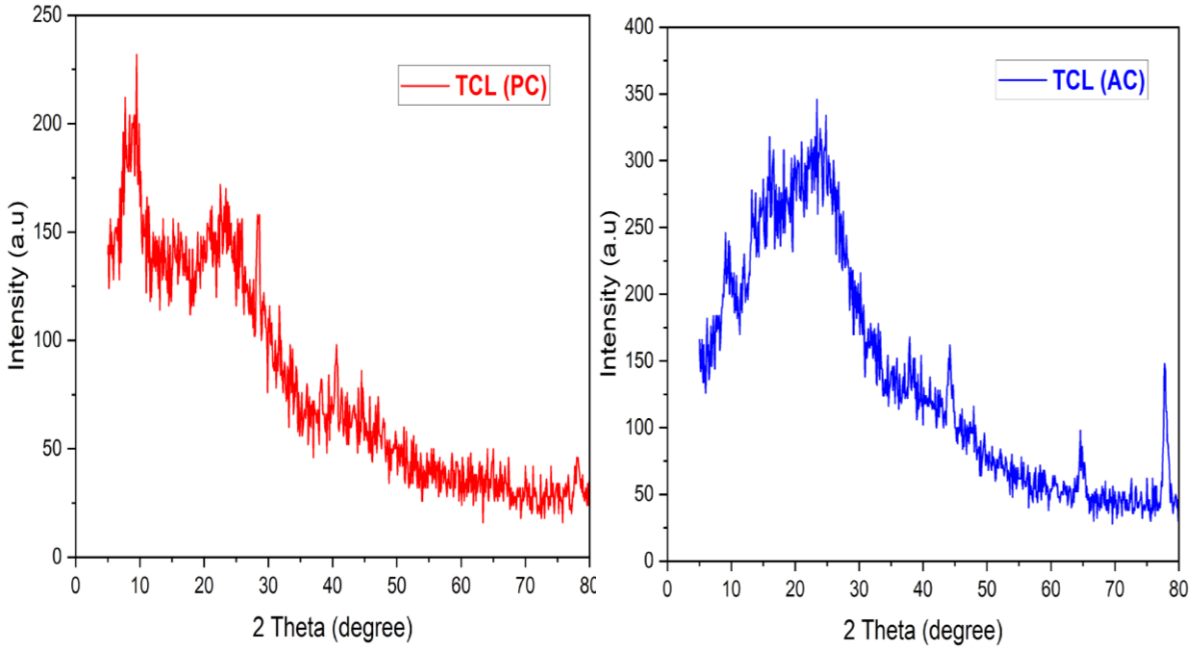


Fig: 4.11 XRD values obtained in PC and AC-TCL

From the Fig: 4.11, XRD is amorphous nature and the diffraction peak for PC-TCL was observed at 2Θ = 23.3° with the d-spacing of 3.81 A° with reflection around (002) plane of graphite suggesting the formation of carbon product with a limited degree of graphitization **(Wang *et al.*, 2017)** whereas in the AC-TCL, 2Θ = 22.3°, 44° may be designated to (002) plane of disordered carbon layer. Furthermore, an intense peak at 2Θ = 77.8° with d spacing of 1.2 A° with crystallite size of 14.38 nm corresponds to the (110) plane was observed.

We can conclude that, after activation crystalline size is enhanced and it will improve the conductivity of activated carbon materials **(Sofia Jeniffer Rajasekaran *et al.*, 2020)**.

Carbon materials	**Position (2Θ)**	**FWHM(2Θ)**	**d-Spacing (A°)**	**Crystallite size (nm)**
PC-TCL	28.5750	1.55000	3.12131	5.53
AC-TCL	77.8147	0.74200	1.22647	14.38

Table 4.7: Crystalline size of PC and AC-TCL

From the table 4.7, the crystalline size of PC and AC-TCL were found to be 5.53 and 14.38 nm. (XRD Crystallite (grain) Size Calculator (Scherrer Equation) - InstaNANO. https://instanano.com/characterization/calculator/xrd/crystallite-size/)

4.2.6 Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA):

The amount and rate of weight changes in any carbon materials were measured by using TGA either as a function of temperature with increasing temperature or isothermally as a function of time. It was used to characterize any carbon material which exhibits a weight change and detects phase changes due to oxidation, decomposition or dehydration. DTA was used for determining the nature of reactions whether it is exothermic or endothermic.

a) TGA profiles of PC and AC-PPL:

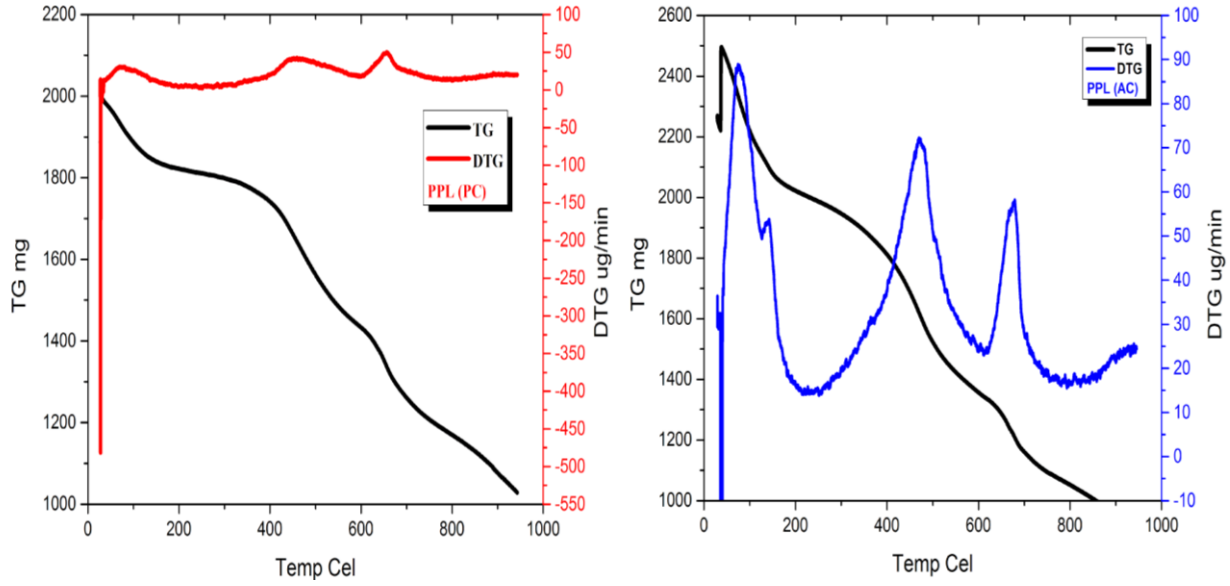


Fig: 4.12 TGA images of PC and AC-PPL

From the TGA profiles of PC and AC-PPL, it was identified that in PC-PPL initial weight loss at 100°C was due to the physically adsorbed water molecules and moisture. **(Sudhan Nagarajan *et al.*, 2016)** and a secondary weight loss around 500°C was due to the degradation of cellulose and hemicelluloses **(Giulyane Felix de Oliveira *et al.*, 2016)** whereas in AC-PPL, the initial weight loss was observed at 100°C and secondary weight loss was observed around 450°C is due to the decomposition of carbon **(Sudhan Nagarajan *et al.*, 2016).**

DTA profile of PC and AC-PPL:

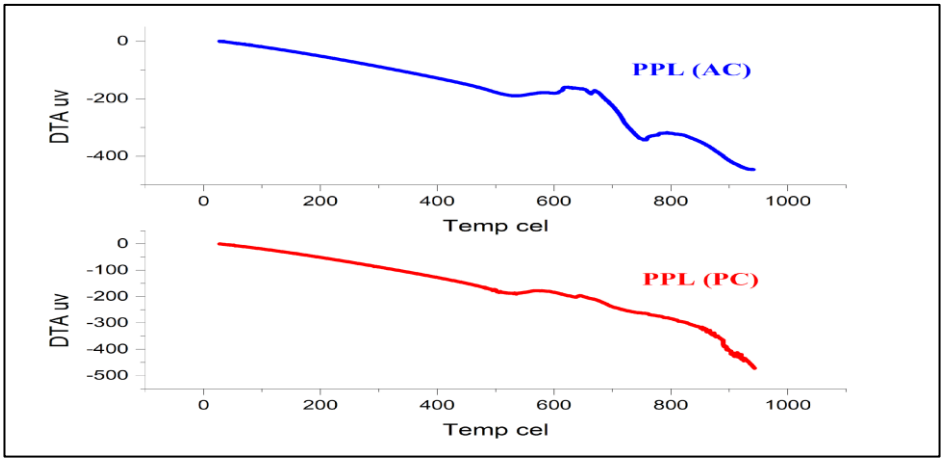


Fig: 4.13 DTA images of PC and AC-PPL

From the DTA profiles of PC-PPL, it showed that the reaction is exothermic in nature with weight loss of 16.6 % at around 100-400°C and a weight loss of 21.5 % at around 450-800°C whereas in the AC-PPL, there was a slight endothermic reaction with absorption of small amount of energy then around 700-800°C it undergone exothermic reaction with mass loss of 23.5% at around 100-350°C and a weight loss of 30.3 % at around 400-800°C.

b) TGA profiles of PC and AC-TCL:

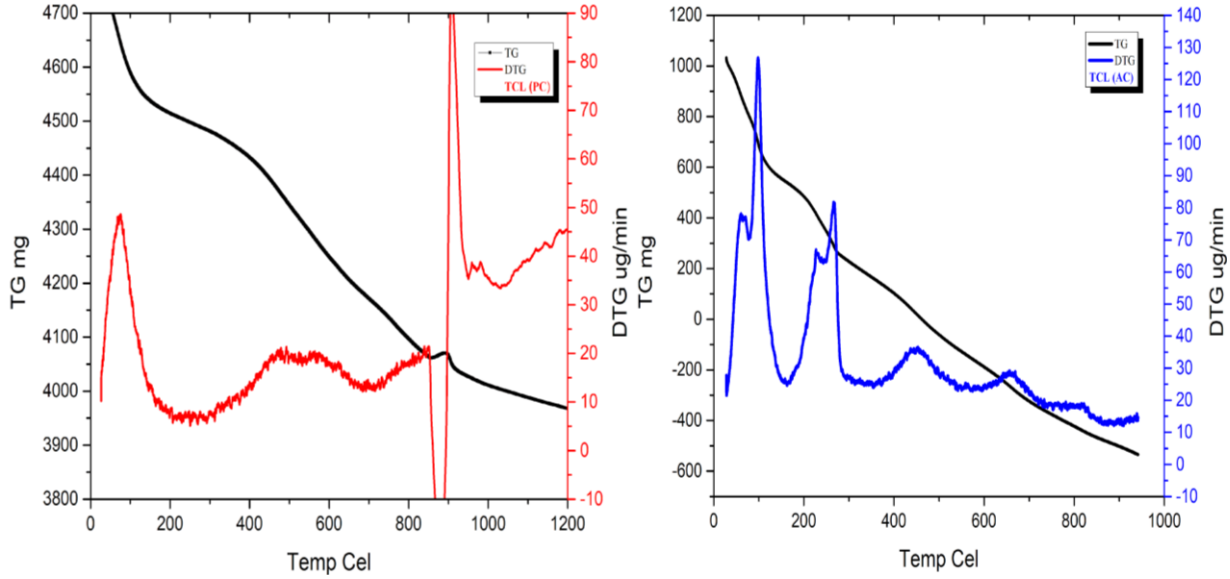


Fig: 4.14 TGA images of PC and AC-TCL

From the TGA profile of PC-TCL and AC-TCL, it was observed that in PC-TCL, initial weight loss at 100°C was due to the physically adsorbed water molecules and moisture **(Sudhan Nagarajan *et al.*, 2016)** and a gradual decrease of organic matter at about 200°C whereas in the AC-TCL, initial weight loss was observed at 100°C and weight loss around 450°C was due to the decomposition of carbon.

DTA profile of PC and AC-TCL:

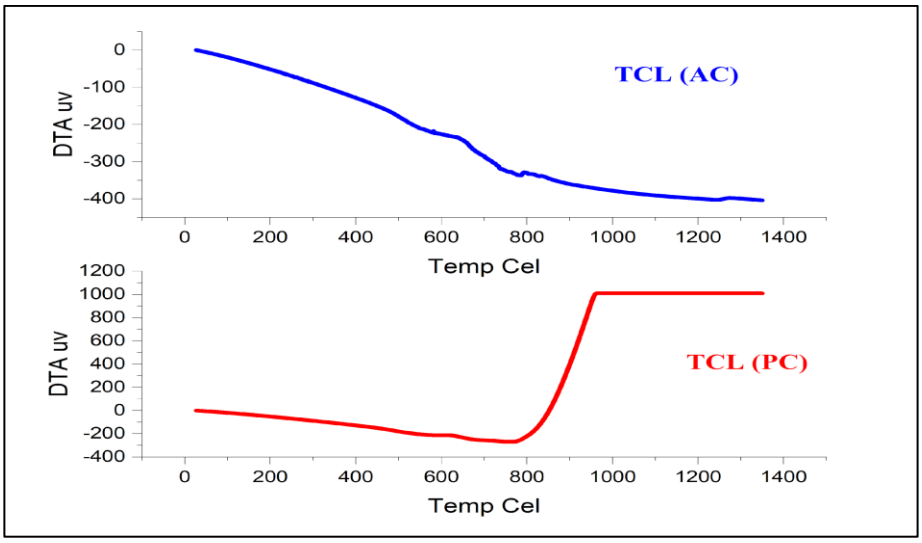


Fig: 4.15 DTA of PC and AC-TCL

From the DTA profiles of PC-TCL, it showed that the reaction is endothermic in nature with a weight loss of 6.6% at around 100-400°C and a weight loss of 6.9% at around 450-1000°C whereas in the AC-TCL, it undergone slight exothermic reaction around 600°C with weight loss of 72.2% at around 100-300°C and a weight loss of 54.5% at around 350-800°C.

4.2.7 Comparison of Crystallite size in synthesized carbon materials:

Crystallite size or grain size of as synthesized pre-carbonized and activated carbon materials were calculated using Raman spectroscopy and XRD techniques.

Carbon materials	**Crystalline size (nm)**	
	Raman spectroscopy	**XRD**
PC-PPL	18.41	11.98
AC-PPL	17.82	14.95
PC-TCL	17.82	5.53
AC-TCL	18.82	14.38

Table 4.8 : Crystallite size of synthesized carbon materials

The crystalline size of synthesized pre-carbonized and activated carbon materials were shown in table 4.8, it was found that the maximum crystalline size were in the range of 5.53-18.41 nm.

5. SUMMARY AND CONCLUSION

This research focused on the green and environmentally friendly synthesis of activated carbon materials using natural precursors such as leaves of *Plumeria pudica* and *Tecoma capensis* by a new facile and energy consuming microwave-assisted activation method with the help of KOH as activating agent. The synthesized pre-carbonized and activated carbon materials were characterized using various techniques such as UV, FTIR, Raman spectroscopy, XRD and TGA.

- Absorption in 250-290 nm range has confirmed the formation of carbon materials which was related to electronic transitions between the bonding and antibonding π orbitals.
- XRD results shows that the prepared carbon materials were amorphous in nature and it was found that, KOH activation enhanced crystalline size and it will enhance the conductivity of activated carbon materials by enhancing ion transport.
- TGA analysis shows the elimination of physically adsorbed water molecules at 100°C followed by other organic substances.
- FTIR results infers the presence of O- and N- functionalities in the synthesized carbon materials. The existence of nitrogen and oxygen containing surface functional groups can increase the electrical conductivity.
- Raman spectroscopy reveals that the performance of carbon materials not only depends on the activation process but also depends on the type of precursors chosen. It was seen that, AC-PPL has higher I_D/I_G value than PC-PPL, which indicates that KOH activation leads to lower the graphitization degree whereas in AC-TCL, the I_D/I_G value reduced from 0.94 to 0.89 than PC-TCL, which confirmed the reorientation of defective sites. It was concluded that the synthesis of carbon materials also depends on the type of precursors chosen.
- The existence of nitrogen and oxygen functionalities, enhanced crystalline size in activated carbon materials that will play a key role in supercapacitor performance as observed by several researchers.

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