PRODUCTION AND CHARACTERIZATION OF ACTIVATED CHARCOAL FROM COCOA POD

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TAVANUR - 679573, MALAPPURAM

KERALA, INDIA

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THESIS

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KELAPPAJI COLLEGE OF AGRICULTURAL ENGINEERING AND TECHNOLOGY

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KERALA, INDIA

2023

DECLARATION

We hereby declare that this project report entitled "**PRODUCTION AND CHARACTERIZATION OF ACTIVATED CHARCOAL FROM COCOA POD**" is a bonafide record of research work done by us during the course of research and that the report has not previously formed the basis for the award to me of any degree, diploma, associateship, fellowship or other similar title, of any other University or Society.

Place: Tavanur

Date :

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CERTIFICATE

Certified that this project entitled "**PRODUCTION AND CHARACTERIZATION OF ACTIVATED CHARCOAL FROM COCOA POD**" is a bonafide record of project work jointly done by **Haritha H (2019-06-009), Joseph PJ (2019-06-010), Malu S (2019-06-011), Megha (2019-06-013) & Sharon Shaji (2019-06-019)** under my guidance and supervision and that it has not previously formed the basis for the award of any degree, diploma, fellowship or associateship to them.

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Haritha H

Joseph PJ

Malu S

Megha

Sharon Shaji

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SYMBOLS AND ABBREVIATIONS

%	-	percentage
&	-	and
/	-	per
=	-	equal to
±	-	Plus or minus
º	-	latitude
ºC	-	degree Celsius
cm	-	centi metre
µm	-	micro metre
nm	-	nano metre
Å	-	angstrom
AC	-	Activated charcoal
ASTM	-	American Society for Testing and Materials
AOAC	-	Association Of Official Agricultural Chemists
BOD	-	Biochemical oxygen demand
BET	-	Brunauer-Emmett-Teller
CAGR	-	Compound annual growth rate
CRD	-	Completely Randomaised Design
dept.	-	Department
et.al	-	and others
Fig.	-	figure
g	-	gram
kg	-	kilogram
g/kg	-	gram per kilogram
ha	-	hectare

hr	-	hour
K	-	kelvin
KCAET	-	Kelappaji College of Agricultural Engineering and Technology
KAU	-	Kerala Agricultural University
m	-	metre
M	-	molarity
Max.	-	Maximum
MC	-	Moisture content
min.	-	minute
mm	-	millimetre
mg	-	milligram
mg/L	-	milligram per litre
m^2/g	-	(metre square) per gram
mEq/kg	-	Milliequivalence per kilogram
N	-	Normality
OPF	-	Oil palm fibre
pH	-	Potential of hydrogen
PKS	-	Palm kernel shell
ppb	-	Part per billion
SEM	-	Scanning electron microscope
t/ha	-	tonnes per hectare
TSS	-	Total suspended solid
USD	-	United States Dollar
UV	-	Ultra violet
viz.,	-	namely
wb	-	Wet basis

Wt.	-	weight
XRD	-	X-ray diffraction

INTRODUCTION

CHAPTER I

INTRODUCTION

Cocoa (*Theobroma cacao L.)* is an evergreen tropical crop also known as the fruit of God. The plant is native to amazon regions of south America & was consumed by humans as early as 5,000 years ago. It grows in tropical environment within 15-20° latitude from equator. Cocoa belongs to the genus theobroma of the family malvaceae. It is grown at an altitude of less than 1312 feet above sea level and optimal temperatures range between 18ºC and 32ºC and rainfall should be at least 100 cm, but not more than 300 cm per year (Anon, 2008). Coming to the nutrition Cocoa is a highly concentrated food providing approximately 1,000 calories per kilogram, provides carbohydrates, fat, protein and minerals. Its theobromine and caffeine content produce a mildly stimulating effect. The carbohydrates are easily digested fats which make them an excellent high-energy food.

The global cocoa processing market size reached 4.58 MT in 2022. As cocoa butter and powder are used in the manufacturing of chocolate and various other chocolate products, the rising demand for these products is currently driving the growth of the market. The global cocoa processing market is further expected to grow at a CAGR of about 1.3% between 2023 and 2028 to reach a volume of about 4.95 MT by 2028. In terms of share of total world production, Africa is expected to remain by far the largest cocoa producing region, accounting for 77% of world cocoa output. The shares of the Americas and Asia and Oceania are likely to be 17% and 6%, respectively (Anon, 2021).

In India Cocoa is being cultivated in the States of Kerala, Karnataka, Andhra Pradesh and Tamil Nadu in an area of 1,03,376 ha with total production of 27,072 MT. Andhra Pradesh had the highest volume of cocoa production in India in fiscal year 2022, amounting to over 11 thousand metric tons. Kerala followed, contributing 35 percent to the cocoa production share that year, all of which totalled to over ten thousand metric tons. The country has exported 27,318.76 MT of Cocoa products to the world for the worth Rs. 1,145.50 Crores per 153.64 USD Millions during the year 2021-22.

There are three large and distinct groups within the species of cocoa. These are the traditional two races–Criollo and Forastero and the third derived group –Trinitario. The cocoa fruit consists of three main components, viz., pod, placenta and bean. The pod is the largest part of the cocoa fruit and occupies more than 70% of the weight of the ripe cocoa fruit. The

percentage of cocoa beans is about 27-29%, the remainder being the placenta that connects 30-40 beans (Wood and Lass 1985).

Cocoa beans from cocoa is the main raw material in the production of chocolates, cosmetics, health drinks etc. Cocoa butter is also used in the production of pharmaceutical products (Opeke, 1987). The cocoa bean powder is the raw material for the preparation of chocolates, ice-cream, soft drinks and confectionaries. But cocoa pod still being the largest part and occupying 70% of the cocoa fruit is wasted simply. But the major by product cocoa pod are used inefficiently causing extensive pollution to the environment. It will be a great advantage if this cocoa pod can be used efficiently. Cocoa pod contain 51.98% lignin, 21.06% hemicellulose, 20.15% cellulose, 6% pectin, 0.15-0.4% theobromine. It cannot be used as animal feed because lignin is indigestible in animals. But cocoa pod can be converted to Activated Charcoal that has wide range of application in numerous industries. Activated Charcoal also known as Activated Carbon is the charcoal that has been heated or otherwise treated to increase its adsorptive power. It is processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reaction.

Depending on the source material, and the processing methods used to produce activated charcoal, the physical and chemical properties of the end product can differ significantly. Because of this, commercially produced activated charcoals are highly specialized to achieve the best results for a given application. Despite such variation, there are three main types activated charcoal are powdered activated charcoal, granular activated charcoal and extruded activated charcoal.

Along with the growth of large and small industries around the world, the need for activated carbon was increasing. Activated charcoal can be used as an ingredient in deodorizers (deodorizing), fuel, filters, energy producers (batteries, solar panels), fine arts media, fillers and dyes and as a material for thermoelectric.

Considering the above facts, a study had been undertaken at KCAET, Tavanur on "**Production & Characterization of Activated Charcoal from Cocoa Pod"** with the following objectives;

- To optimize the process protocol for the production of activated charcoal from cocoa pod.
- Characterization of the produced activated charcoal.
- To study the effect of separated activated charcoal in the purification of oil and water.

REVIEW OF LITERATURE

CHAPTER - II

REVIEW OF LITERATURE

This chapter contains reviews of researches related to production and characterization of activated charcoal from cocoa pod. This chapter also provides general information related to cocoa , activated charcoal and its applications.

2.1. Cocoa

The cocoa tree, *Theobroma cacao L.*, originated in the tropical regions of South America. Later on, the cultivation is spread to other countries viz., Central America, Mexico, West Africa and South East Asia, where the climatic condition is ideal (Ardhana and Fleet., 2003). It proliferates in the tropical climate, 20° North and South of the equator. It grows in humid areas with average annual rainfall and relative humidity of 1250-3000 mm and 70-100%, respectively. Cocoa trees are multiplied by vegetative propagation through budding or grafting. The trees are 12 -15 meter in height and are often grown as an intercrop. The cacao trees are fast-growing and start bearing pods after two to three years (Cook., 1982; Beckett., 2009).

Cacao grows in the forest understory to a height of 6 -12 metre (20 - 40 feet), usually remaining at the lower end of this range. It's oblong leathery leaves measure up to 30cm (12 inches) in length, and are periodically shed and replaced by new leaves that are strikingly red when young. Its flowers are either foul-smelling or odourless; they can be present at all times but appear in abundance twice a year. These flowers grow in clusters directly from the trunk and limbs and are about 1cm (0.4 inch) in height and breadth. After four years the mature cacao tree produces fruit in the form of elongated pods; it may yield up to 70 such fruits annually. The fruit is fully grown in 143 days and after the ripening starts. Maturity is attained after 170 days as indicated by the colour of the pod walls. Harvesting is done twice a year. On an average a fruit is 180 – 200 mm long and weighsabout 400 to 500 g. The pods, or cherelles, range in colour from bright yellow to deep purple. They ripen in less than six months to a length up to 35cm (14 inches) and a width at the centre of 12cm (4.7 inches). Each pod has numerous ridges running along its length and holds 20 to 60 seeds, or cocoa beans, arranged around the long axis of the pod. The oval seeds are about 2.5 cm (1inch) long and are covered with a sweet sticky white pulp. Harvesting of cocoa beanscan proceed all year, but the bulk of the crop is gathered in two flush periods occurring from October to February and from May to August.

2.1.1. History

Plant was consumed by humans as early as 5,000 years ago. The tree was likely domesticated in the upper Amazon region and then spread northward. It was cultivated more than 3,000 years ago by the Maya, Toltec and Aztec peoples, who prepared a beverage from the bean. The cocoa tree is native to the South America. It may have originated in the foothills of the Andes in the Amazon and Orinoco basins of South America, current day Venezuela, where even today, wild cocoa variety still can be found. However, it may have had a larger range in the past, evidence for which may be obscured because of its cultivation in these areas long before, as well as after, the spanish arrived. It was first cultivated by the Olmecs at least 1500 BC in Central America. Chocolate was introduced to Europe by the Spaniards, and became a popular beverage by the mid-17th century. The cocoa plant was first given its botanical name by Swedish natural scientist Carl Linnaeus in his original classification of the plant kindom, who called it Theobroma (“ Food of the Gods”) cacao (Anon, 2015).

2.1.2. Cocoa Production

Globally, eight country are regarded as major cocoa bean producers. Fig 2.1 shows the production status of cocoa during 2021-2022. The total world production of cocoa in 2021-2022 was 4.9 MT.

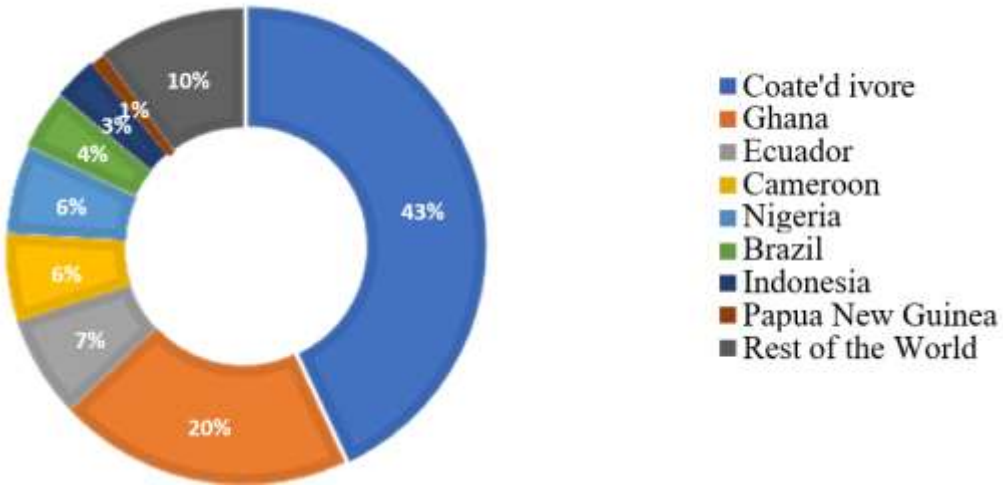

Fig 2.1. World Cocoa Production (%) in 2021-2022

Source: ICCO

Coate’d ivore and Ghana are by far the two largest cocoa growing countries, accounting for over 60% of global cocoa producion, followed by Ecuador with 7%. In Asia, Indonesia is the largest producer country.

In India cocoa is being cultivated in the States of Kerala, Karnataka, Andhra Pradesh and Tamil Nadu in an area of 1,03,376 ha with total production of 27,072 MT. Andhra Pradesh had the highest volume of cocoa production in India in fiscal year 2022, amounting to over 11 thousand metric tons shown in Fig 2.2 . Kerala followed, contributing 35 percent to the cocoa production share that year, all of which totalled to over ten thousand metric tons. The country has exported 27,318.76 MT of Cocoa products to the world for the worth Rs. 1,145.50 Crores per 153.64 USD Millions during the year 2021-22.

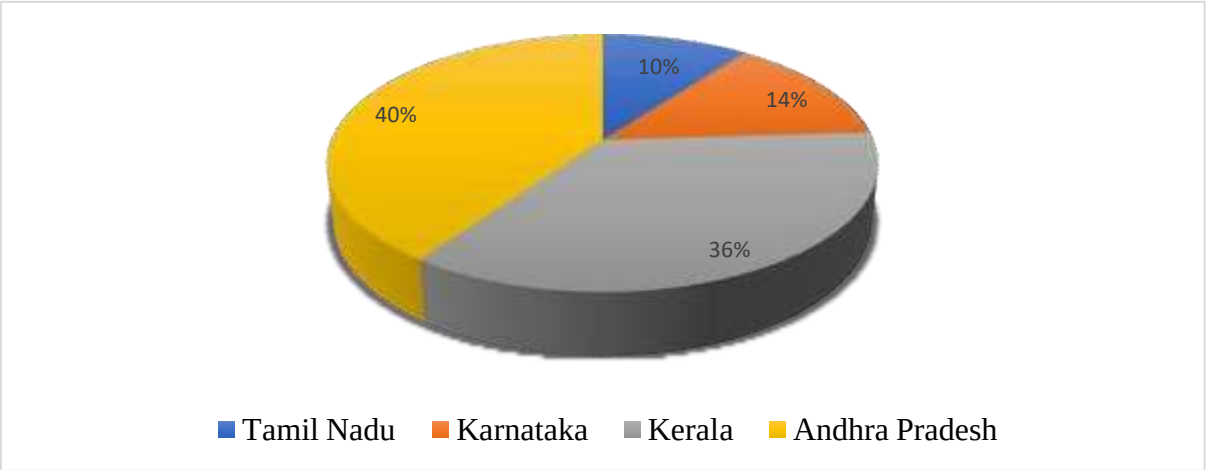

Fig 2.2. Cocoa production (%) in India 2021-2022

Source: Statista Research Department

2.1.3. Varieties of Cocoa

The three large and distinct groups within the species *cacao* are *Criollo*, *Forastero and Trinitario.* shown in Fig 2.3

2.1.3.1. Criollo

It is native to central America and considered the best flavoured cocoa. This variety has white to pale yellow cotyledon. Some types produce a jorquette, while others do not. The variety is also characterized by slender trees, green pods or pods coloured by a anthocyanin pigments. Leaves are relatively smaller and more oval than the other types. The seed is cylindrical and plumb. It weighs around one gram and is covered with sweet mucilage. Pods are soft, easy to break and don not have the woody layer found in other varieties. Immature pod colour ranges from pale green to red. On fermentation and drying the cotyledon colour turns light brown.It is very susceptible to most pests and diseases of cocoa. It produces the bestquality chocolate. With proper attention and care, the yield can be enhanced high as 1.0 – 1.5 t/ha. (Adewumi, 1997).

2.1.3.2. Forastero

Forastero is native to Venezuela and Northern Amazon Basin. It is commercially grown in Brazil, Central America, the Caribbeans and West Africa. The group is characterized by green pods, absence of anthocyanin pigmentation, thick pericarp, strongly lignified mesocarp, plump but slightly flattened purple beans. The trees are vigorous, with leaves larger than those of criollo. Forastero is noted for its precocity, superior growth vigour, and high bean yields as well as appreciable and tolerance to West African virus strains. (Adewumi, 1997).

2.1.3.3. Trinitario

Trinitario is a product of hybridization between criollo and forastero has its origin in Trinidad. It show a range of characteristics possessed by both criollo and forastero. The trees are generally vigorous with a variable reaction to pests and diseases. Pods are green or pigmented. Beans colour varies from light to very dark purple. Most of the present cocoa on farmers' fields in Nigeria and indeed many parts of West Africa seem to be hybrid types. The most useful and valuable part of the crop is the bean. The highest percentages of cocoa beans produced in the developing countries are exported. The exported beans are processed abroad and the end products are imported back to the developing countries at a relatively high cost (Adewumi, 1997).

Fig 2.3. Varieties of Cocoa

source : Bar and cocoa

2.1.4. Propagation

Cocoa is grown from seed or propagated from upright stem cuttings possessing 2 to 5 leaves and including 1 to 2 buds. The cutting should be taken early in the morning and the leaves cut to about half their length and then dipped in a rooting hormone and placed in a small container filled with moist, clean, well-draining, soil media. The cutting should then be covered with a polyethylene bag and placed in a warm but shaded area. The soil should be kept moist

but not overly wet. Rooting should take place in about 4 weeks, during which time the bag may be slowly opened. Once the plant is fully rooted and growing, it may be moved repeatedly to increasing light levels. Cocoa may also be propagated by marcottage (airlayering) and budding and grafting (Jonathan *et al*., 2012).

2.1.5. Structure of cocoa

The cocoa pod consists of pod, beans, placenta and mucilaginous pulp. Cocoa pods are usually ovoid in shape and can range from 20 to 32 cm in length. The colour ranges from yellow to red or violet. The surface texture of most cocoa pods is deeply grooved to nearly smooth. Cocoa bean is encompassed by mucilaginous pulp. The number of beans per pod ranges between 30 and 40. Bean consists of two convoluted cotyledons and a germ, all enclosed in the testa. The colour of the cotyledon varies from white to purple (Adzimah and Asian, 2010). The schematic diagram of cocoa pod is shown in Fig. 2.4

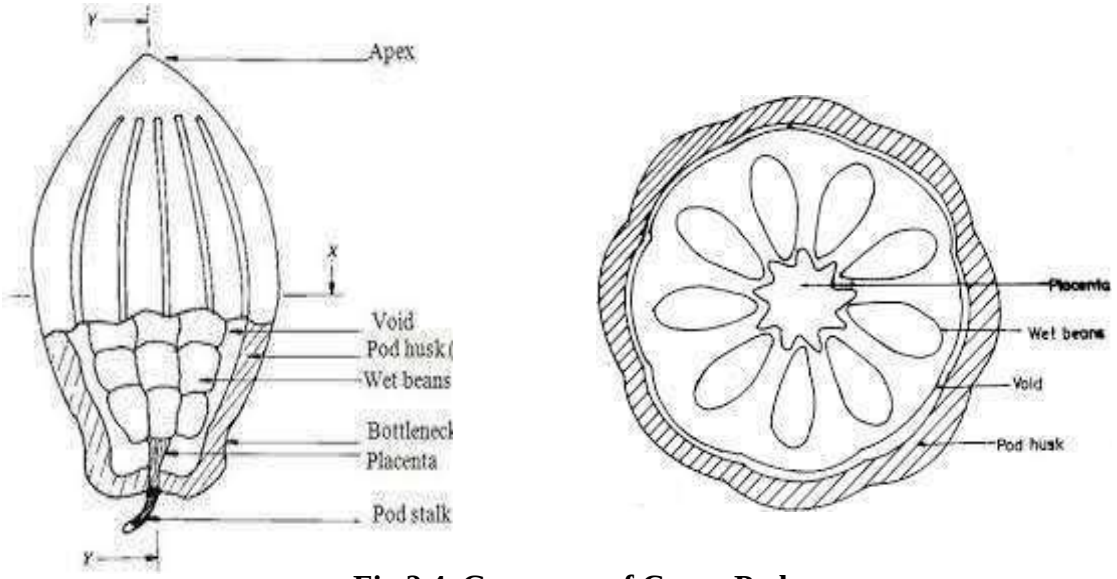

Fig 2.4. Geometry of Cocoa Pod

Source: Fabunmi, (2004)

2.1.6. Biochemical composition of cocoa pod husk, shell and beans.

The physical and chemical characteristics of hybrid varieties of cocoa were determined by Padilla *et al.,* (2000). The proximal composition, physical and chemical characteristics as well as the fatty acid profile the cocoa beans were estimated using AOAC methods. The result after values from 3.37 ± 0.10 to 3.86 ± 0.05g /100g. The fat content values ranged from 47.27± 0.14 to 54.21 ± 0.58g/100g with an average of 51.51 ± 0.18g/100g and there were significant differences among all cultivars. The crude fiber content variation was between 5.69 and 8.79g/100g.

The carbohydrate content for these hybrids presented an average of 21.65g/100g. Cocoa pulp is a rich medium for microbial growth. It consists of 82-87 per cent water, 10-15 per cent sugar, 2-3 per cent pentosans, 1-3 per cent citric acid and 1-1.58 per cent pectin. Proteins, amino acids, vitamins (mainly vitamin C) and minerals are also present (Schwan & Wheals, 2004).

Oddoye *et al*., (2010) used fresh cocoa pod husk as an ingredient in the diets of growing pigs and concluded that feeding fresh (wet) cocoa pod husk to growing pigs, up to 300g/kg (dry weight basis) of the diet had no deleterious effects on the pigs. The proximate analysisfor the fresh cocoa pod husk is presented in Table 2.1.

Table 2.1. Proximate analysis of fresh cocoa pod husk

Components	Content
Dry matter (g/kg)	130
Organic matter, g/kg DM (dry mater)	938
Crude protein, g/kg DM	78
Ether extract, g/kg DM	19
Crude fibre, g/kg DM	179
Nitrogen-free extract, g/kg DM	565
Calcium, g/kg DM	8.0
Phosphorous, g/kg DM	4.1

Source: Oddoye *et al*., (2010)

The total phenolic compound content, proximate compositions and biological activity of cocoa bean shell was evaluated by Atindana *et al.,* (2012). The dietary fiber, protein, fat, polyphenols and moisture present in cocoa bean shell were 50, 16.93, 6.87, 4.85 and 3.73 per cent, respectively. Due to higher dietary fiber content, it has wide applications in confectionery, bakery or in the preparation of low fat, high fiber dietetic products.

The proximate analysis of pulp and seed of fresh cocoa beans as determined by various researchers are consolidated and given in Table 2.2.

Table 2.2. Proximate analysis of fresh cocoa beans (pulp and seed)

Component	Average concentration (per cent w/w)	
	Pulp	Seed
Water	80-85	35-45
Lipid	<0.5	45-55
Sugars(sucrose, glucose and fructose)	10-16	0.5-2
Polysaccharides	1.5-3	14-20
Pectin	4-7	2.0
Protein	0.6	1.5-1.7
Organic acids (citric acid)	1-3	0.3-0.9
Inorganic salt	0.5-1.0	0.5-1.0
Polyphenols	<0.1	7-10
Alkaloids (theobromine and caffeine)	<0.1	3-3.5

Source: Thompson *et al*., (2001); Ardhana and Fleet (2003); Schwan and Wheals (2004)

2.2. Activated Charcoal

Activated charcoal (AC) is composed of carbon arranged in a quasi-graphitic form in small particle size. It is a porous and tasteless material and is distinguished from elementary carbon by removal of all noncarbon impurities and the oxidation of carbon surface (Budavari 1996; Mattson & Mark, 1971). AC has a very fine network of pores, an extraordinarily large surface area and volume that gives it a unique adsorption capacity (Baker *et al*., 1992).

Activated charcoal is a very porous, soft, black substance made by heating materials containing carbon within a restricted amount of air. These are most often derived from hardwood trees and coconut shells. Charcoal adsorbs 100 to 200 times its own weight. The adsorption capacity is developed by activating the charcoal through heating (Fishel *et al*., 2008).

Activated carbon, also known as activated charcoal, is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions. It has high degree of microporosity. The surface area may vary greatly

depending upon precusor (raw material) and the condition of carbonization for making active carbon. As determined by gas adsorption, people used activated charcoalshaving surface area like 1500 and 3,000 m^2/g in their research work, (Dillon *et al*., 1989).

2.2.1. Pore Structure

Activated charcoal can be defined as a crude form of graphite with a random or amorphous structure, which is highly porous over a broad range of pore sizes, from visible cracks and crevices to cracks and crevices of molecular dimensions. Activated charcoal purification is primarily based on a phenomenon called adsorption, in which molecules of a liquid or gas are trapped by either an external or internal surface of a solid. The phenomenon is some what similar to iron filings being held by a magnet. Activated charcoal has a very high internal surface area (up to 1500 m^2/g) and is thus an ideal material for adsorption.

Activated charcoal can be manufactured from a wide variety of raw materials containing a high percentage of carbon. The production process of converting the raw material into the finished adsorbent can be divided into chemical and thermal processes both of which require the use of elevated temperatures.

The pore structure of activated charcoal varies and is largely as a result of the source materialand the method of production. The pore structure, in combination with attractive forces, is whatallows adsorption to occur. The volume of the pores in activated carbons is generally defined as being greater than 0.2 ml/g, and the internal surface area is generally larger than 400 m^2/gasmeasured by the nitrogen BET method.

According to the IUPAC (International Union of Pure and Applied Chemistry), three groups of pores are distinguished, according to the pore size:

Macropores: (> 50 nm diameter)

Mesopores: (2-50 nm diameter)

Micropores: (< 2 nm diameter)

Micropores generally contribute to the major part of the internal surface area. Macro and mesopores can generally be regarded as the highways into the carbon particle, and are crucial for kinetics, (nitsri.ac.in).

2.2.2. Preparation and Characterisation of Activated Charcoal

Making activated charcoal can be done in two stages. The first stage was carbonization of raw materials by pyrolysis to produce carbon. The second stage was activated process to

remove hydrocarbons that line the carbon surface so as to increase carbon porosity. Carbonization was an imperfect combustion process of organic matter which composes the structure f the material in the form of cellulose, hemicellulose and lignin with a limited amountof oxygen that produces carbon.

Activated charcoal was a solid containing 85-95% carbon produced from carbon containing materials by heating at high temperatures. Activated charcoal was shaped like amorphous which has a large surface area and porous volume. The amount of activated charcoal produced was determined by the initial composition of biomass, the more volatile substances the more active carbon was produced because many parts are released into the air. Activated of forming and composing carbon so that the pores become larger and remove impurities in the pores of the activated carbon by breaking the hydrocarbon bonds, (nitsri.ac.in).

Carbon activation can be done in two ways, namely physical activation and chemical activation. On physical activation, carbon was activated at temperatures between 800°C-1000°C by using steam or gas such as water vapor. In chemical activation, carbon was activatedthrough a process of soaking with chemicals before being heated. Chemicals that can be used are H_3PO_4, NH_4CI, $AICI_3$, HNO_3, KOH, NaOH, $KMnO_4$, SO_3, K_2S and HCI, (Putra,2019).

Ulfah & Putra (2019) prepared and characterized activated charcoal from cocoa shell (*Theobroma cacao L*). Carbon from cacao shells was prepared by pyrolysis method at 300°C for 1hr. This carbon was activated by chemical activation process with various activating reagent and concentration. The best activating reagent was HCl with concentration of 4N that improved the bounded carbon to 91.78%. The water content, ash content, and vapor content of activated carbon was obtained as follows, 1.59%, 0.0598% and 8.33%.

Evbuomwan *et al.,* (2013) conducted a comparative study of physio-chemical properties of activated carbon of oil palm waste (PKS & OPF). The properties evaluated were surface area, moisture content, pH, bulk density, pore volume, porosity, tortuosity, ash content and metal ions present in the oil palm waste. From the analysis the physio-chemical properties of activated carbon of PKS and OPF were, moisture content (2.15% & 3.34%), ash content (6.10% & 6.7%), surface area ($1080m^2/g$ &$1030m^2/g$), pH (6.7 & 6.6), bulk density (0.64 & 0.56), porosity (63.6% & 57.9%), pore volume ($0.69cm^3/g$ & $0.58cm^3/g$) and tortuosity (1.57 & 1.72).

2.2.3. Types of activated carbon

Depending on the source material, and the processing methods used to produce activated charcoal, the physical and chemical properties of the end product can differ significantly. This creates a matrix of possibilities for variation in commercially produced carbons, with hundreds of varieties available. Because of this, commercially produced activated carbons are highly specialized to achieve the best results for a given application. Despite such variation, there are three main types (Fig 2.5) of activated charcoal produced:

- Powdered Activated Charcoal (PAC)
- Granular Activated Charcoal (GAC)
- Extruded Activated Charcoal (EAC)

a **b** **c**

Fig 2.5. Types of AC (a – PAC, b – GAC & c – EAC)

Source : NITSRI

2.2.3.1. Powdered Activated Charcoal (PAC)

- Powdered activated charcoal generally fall in the particle size range of 5 to 150 Å with some outlying someoutlying Sizes available**.**
- PACs are typically used in liquid-phase adsorption applications and offer reduced processing costs and flexibility in operation, (nitsri.ac.in).

2.2.3.2. Granular Activated Charcoal (GAC)

- Granular activated charcoal generally range in particle sizes of 0.2 mm to 5 mm and can be used in both gas and liquid phase applications.
- GACs are popular because they offer clean handling and tend to last longer than PACs.
- Additionally, they offer improved strength (hardness) and can be regenerated and reused.

2.2.3.3. Extruded Activated Charcoal (EAC)

- Extruded activated charcoal are a cylindrical pellet product ranging in size from 1 mm to 5 mm.
- Typically used in gas phase reactions, EACs are a heavy-duty activated carbon as a result of the extrusion process.

Along with the growth of large and small industries around the world, the need for activated charcoal was increasing. Activated charcoal can be used as an ingredient in deodorizers (deodorizing), fuel, filters, energy producers (batteries, solar panels), fine arts media, fillers and dyes and as a material for thermoelectric. Activated charcoal can be produced from agricultural waste such as fruit peels, bark, shell, husk and others.

Making activated charcoal can be done in two stages. The first stage was carbonization of raw materials by pyrolysis to produce carbon. The second stage was activated process to remove hydrocarbons that line the carbon surface so as to increase carbon porosity. Carbonization was an imperfect combustion process of organic matter which composes the structure of the material in the form of cellulose, hemicellulose and lignin with a limited amount of oxygen that produces carbon.

Activated charcoal was a solid containing 85-95% carbon produced from carbon containing materials by heating at high temperatures. Activated charcoal was shaped like amorphous which has a large surface area and porous volume. The amount of activated charcoal 7 produced was determined by the initial composition of biomass, the more volatile substances the more active carbon was produced because many parts are released into the air. Activated of forming and composing carbon so that the pores become larger and remove impurities in the pores of the activated carbon by breaking the hydrocarbon bonds, (nitsri.ac.in).

2.2.4. Characterization of Activated Charcoal

Activated charcoal were characterized by selected physical and chemical properties.

2.2.4.1. Iodine Number

M. Madadi Yeganeh *et al*., (2006) describes that iodine number of the prepared activated carbon was measured by titration at 30°C based on the standard method (ASTM Designation D 4607-94). This parameter was used to evaluate the activated charcoal adsorption capacity.

According to Liu *et al*., (2020) iodine number determination were done by titration and UV–vis spectroscopy according to ASTM D4607-14, GB/T12496.8, and JIS K1474:14, respectively. This method is of importance for quantitative analysis of carbon materials.

2.2.4.2. Surface Area Measurement

The surface area (SBET) of activated charcoal was measured by N_2 adsorption at 77 K using a Quantachrom AUTO ZORB-1. Before measuring the isotherm the samples were heated at 200°C for 2 h in vacuum for degassing (Tahereh Kaghazchi1 *et al*., 2006).

Wenyuan *et al*.,(2019) checked the effect of surface properties of activated charcoal for malachite green adsorption. The activated charcoal were used in this study were purchased from Yantai general activated charcoal co. and termed coconut-AC, coal-AC, apricot-AC and peach-AC based on their origins. They were ground and sieved to 20-40 mesh, and then subjected to acid-washing with 10% HCl and 12% HF at 60°C for 24hr. The treated activated carbons were washed with de-ionized water until pH reached 7 and dried at 150°C for 2hr. It was found that the MG adsorption capacity presented a positive linear relationship with the total specific surface area, which can be used as a key parameter to estimate the adsorption performance of MG on activated carbon.

2.2.4.3. Bulk Density

Apparent or bulk density is a measure of the weight of material that can be contained in a given volume under specified conditions. The volume used in this determination includes, in addition to the volume of the skeletal solid, the volume of the voids among the particles and the volume of the pores within the particles. A 10 ml cylinder was filled to a specified volume with activated carbon that had been dried in an oven at 80°C for 24hr. The cylinder was weighted. The bulk density was then calculated as :

Bulk density = [weight of dry material (g)/volume of packed dry material (ml)]

The volume of this vessel was calibrated by measuring the volume of water at ambient temperature that the vessel can contain (Yeganeh *et al*., 2006)

Madu & Lajide determined the porosity and bulk density by taking 1g of activated charcoal produced from melon seed husk was dispersed in 20 ml water in a graduated cylinder with the aid of a shaker, this was further centrifuged for 10 min. The resulting volume of the water was read a VT and recorded.

2.2.4.4. Particle Size

For the particle size determination, lots of samples were weighed and placed on top of a set of sieves ranging from 75 to 1.4×10^3µm. The sieves were shaken manually for two minutes, after which the weight percent of the active carbon retained on the sieves and bottom pan was determined. The particle size value obtained in this work for the sample was 22.73µm at 540^{o}C activation temperature. The significance of particle sizes is that it aided the fast diffusion of solvent polluted to get to the active part of the activated carbon or carbonaceous material. The finer the particle size of an activated carbon, the better the access to the surface area and the faster the rate of adsorption kinetics (Madu & Lajide , 2013)

2.2.4.5. Ash Content

Soleimani *et al.,* (2006) stated that ash content (ash %) of an activated carbon is the residue that remains when the carbonaceous portion is burned off. The ash content of activated carbon was determined by standard methods (ASTM Designation D 2866-94) . Approximately 1-2 g of powdered activated carbon was placed into weighted ceramic crucibles. Activated carbon and crucibles were dried for 24hr at 80°C and reweighted to obtain the dry carbon weight. The samples were heated in an electrical furnace at (650 ± 25)°C for 3hr. The crucibles were cooled in a desiccator, and the remaining solids (ash) were weighted. The percent of ash was calculated by:

$$\% \text{ Ash} = [\text{remaining solids wt (g)}/\text{original carbon wt (g)}] \times 100$$

From the rice hulls, pistachio shells, almond shells and walnut shells he found that rice hulls have a high ash content.

2.2.4.6. pH

Yeganeh *et al*., (2006) measured the pH in a suspension of 1g of PAC in 1L of distilled water after a contact time of 24hr at 25°C. pH varies with the materials used for preparing activating charcoal.

Madu & Lajide determined the pH by dissolving 1g of activated charcoal in 3ml of de-ionized water. The mixture was heated and stirred for 3min to ensure proper dilution of the sample. The solution was filtered and out and its pH was determined using a digital pH meter. They founded out the pH also affects the rate of activated carbon adsorption.

2.2.4.7. Moisture Content Determination

1g of the activated carbon sample was collected and dried in an oven for four hours at 150^{o}C, until the weight of the sample became constant. Activated carbon is generally priced on a moisture free basis For many purposes, the moisture content does not affect the adsorptive power of activated carbon, but they obviously dilutes the carbon (Madu & Lajide , 2013)

2.2.4.8. Conductivity Measurement

Conductivity measurements were carried out by the method of Ahmedna (1998). 1% (wt/wt) solution of GAC in water was stirred at room temperature for 20min. Electrical conductivity was measured using an EDT instrument BA 380 conductivity meter with values micro Siemens (μs)(Yeganeh *et al*., (2006)). From the materials he used activated charcoal produced from almond shells showed higher conductivity.

2.2.5. Application of Activated Charcoal

- Activated carbon is an incredibly diverse material that tends itself to thousands of applications through its superior adsorbent capabilities.
- The availability of high surface area of particles possessed by AC as well its adsorptive ability makes it a significant constituent in many industries.
- Industries like; petroleum, fertilizer plants, nuclear, pharmaceuticals, cosmetics, textiles, automobile, and vacuum manufacturing all uses AC. It has found to be good porous materials, which make it very effective in adsorption of solutes from aqueous solutions .
- Food Beverages - Activated carbon is widely used throughout the food and beverage industry to accomplish a number of objectives. This includes decaffeination, removal of undesirable components such as odour, taste, or colour, and more. Treatment of glucose, treatment of sugar syrups, purification of edible oil &fats, treatment of fruit juice concentrate, treatment of lactose & gelatine.
- It has been extensively used for; solvents recovery, separation of gases, dye removal from industrial waste water and as a catalyst in the process of biodiesel production.
- Metals recovery- Activated carbon is a valuable tool in the recovery of precious metals such as gold and silver.
- Medicinal

- Remediation
- Biogas purification
- Air emission purification
- Chemicals (Purification with mobile activated carbon filters)
- Waste Water (Purification with activated carbon)- Waste water is produced during the production process which need to be treated before discharged into a sewer or surface water. Activated carbon is often the appropriate technology for treatment at source as well as in between the various production stages, and for end-of-pipe treatment (e.g. after upstream biological or physicochemical treatment), (nitsri.ac.in).

2.2.5.1. Application of activated charcoal in wastewater treatment

Waste water treatment is the removal of impurities from wastewater before it reaches the natural bodies of water like rivers, lakes and oceans. Water as being one of the essential entity is polluted every day. Water pollution is caused by the drainage of contaminated wastewater into the surface water. Various pollutants are discharged into water bodies from household, industries etc. Before discharging, polluted water must be treated. The release of various dyes from industries to water bodies raises severe environmental problems. Even small amount of dyes in rivers are easily detectable (Robati *et al*., 2016). Nowadays, activated charcoal produced is used as an adsorbent in waste water treatment (Sujiono *et al*., 2022; Martin, 1980).

Odubiyi *et al*., (2012) conducted a study on Wastewater Treatment with Activated Charcoal Produced from Cocoa Pod Husk. Heavy metal effluents are released from refinery which causes huge environmental problems. Cocoa pod husk is a natural adsorbent and is cost effective. Study is conducted on the adsorption of heavy metals like Pb and Cu from effluent water. Activated carbon was prepared from cocoa pod husk, carbonized at 500°C and impregnated with 1.0M HCl at 700°C in muffle furnace for 2hr. The resultant product was tested to adsorb heavy metal in effluent water at different pH, dosage and contact time. Effect of pH variation on adsorption capacity and metal removal percentage could be deduced as the sorption of metal cations increased with increase pH as the metal ion species becomes less stable in the solution. Effect of contact time on adsorption of metal ions increases as the time lapses. Graph shows progressive increase in adsorption at initial time and then gradually decreases as the time passes. Effect of GAC dosage shows a trend of increment in adsorption

capacity with increment in adsorbent dosage (from 1-3g) and then decline as dosage increases. The maximum Pb removal efficiency was 78% at pH of 5.5 at a contact time of 1.9hr and Cu removal was 97% at pH of 5.6 for a contact time of 2hr.

Lestari *et al*., (2020) done a work on Treatment of Water River with Activated Charcoal from Coal and Palm shells as Adsorbent. Water has very important role in supporting household activities like drinking, cooking, washing and other necessities. If it gets polluted causes various diseases. This study aimed to treat polluted river water into water suitable for consumption. Activated charcoal produced using palm shells and coal were used as adsorbents. Carbonisation was done at 500^{o}C for 45minutes. Water quality parameters like dissolved oxygen (DO), biochemical oxygen demand (BOD), total solid suspended (TSS) were tested. The results showed that AC from coal has better ability and quality than AC from palm shells. Various AC characterisation parameters like moisture content, ash content, fixed carbon shows higher quality in AC produced from coal. Water treatment using AC from coal for 6 hrs reduced BOD from 5.11 mg/L1.13 mg/L and TSS from 53 mg/L to 7 mg/L. While the DO parameters remain unchanged.

Sunarto *et al*., (2019) published a paper on Industrial Liquid Discharge Treatment with Activated Carbon Produced from Cocoa Pod Husk. Various solvents, heavy metals and suspended solids are contained in industrial liquid discharge which causes environmental pollution. AC was prepared from cost effective cocoa pod husk to adsorb these metals. The amount of metal pollutants in effluents can be reduced by ACs optimum adsorption capacity. The aim of this investigation was to study about the adsorption of metal cadmium(Cd) with AC from cocoa pod husk. Carbonisation done at 100^{o}C in a muffle furnace for 4 hour and activated with 0.5M NaOH by reflux method until 6^{0}C for 24 hours. Adsorption capacity wastested using different contact time. The maximum Cd removal efficiency was 41.2% at a contact time of 100 minutes. Functional groups involved in biosorption of Ni ions by cocoa pod husk is a group -OH and N-H, which reflects the importance of AC in treatment of industrial liquid discharge. The study concludes result as removal of heavy metal was contact time for variation dependent as the adsorbent capacity and metal removal percentage increases with 100minutes contact time variation of the solution.

Krishna, (2014) conducted research on Cocoa Pod Husk Activated Carbon for Textile Industrial Wastewater Colour Removal. Industrial waste water treatment is one of the main environmental problems. If coloured wastewater from industries are directly emitted to rivers, it interferes with the transmission of sunlight into the stream and reduces the photo synthetic

action. By using agricultural wastes like cocoa pod that are abundantly produced in Kerala, Karnataka, Andhra Pradesh and Tamil Nadu, we can treat waste water. Cocoa pod husk has 70 to 75% of the whole weight of cocoa fruit. During activation millions of pores are produced i.e increasing total surface area up to 1000m^2 per gram of carbon. In this research chemical activation was done using $ZnCl_2$ and characterised for the physico-chemical properties. $ZnCl_2$ was considered as one of the best chemical activating agent based on the highest BET surface area (780m^2/g) and pore volume (0.58m^3/g). This also has lowest ash content (6.14%)and highest carbon content (86.1%) compared with other chemicals. These also adsorb As (V),up to removal levels of 80% in less than one hour at the experimental conditions applied (initial pH 6-7, activated carbon concentration 0.5g/l and 1g/l, initial As concentration 100 ppb).

Emahi *et al*., (2019) published an article on Effectiveness of Raw versus Activated Coconut Shells for Removing Arsenic and Mercury from Water. Coconut shell charcoal was activated using $CaCl_2$ and its effectiveness was compared with raw coconut shell powder for removal of Hg and As from contaminated water. From various analyses removal efficiency of Hg and As with the use of AC were 53% and 67%. FT-IR spectroscopy was done to study the similarities and differences in chemical compositions of raw and activated coconut shells before and after biofiltration processes. River water samples are pre-treated with bio-sorbents and various parameters are analysed like (pH, conductivity, colour, TDS and TSS).

Anand Patel *et al*., (2019) conducted a research on Application of Activated Carbon in Wastewater Treatment. From agricultural wastes like coconut shells AC was prepared and chemical activation was done using H_2SO_4. Characterisation of AC were done using FTIR, XRD, SEM analysis. XRD gives sharp peaks which show crystalline structure of AC. Manufactured AC is then used in removal of dyes from textile industrial waste.

Nurhayati *et al*., (2021) done work on Softening of Hardwater using Cocoa Shell Activated Charcoal. Cocoa pod shells contain cellulose, hemicellulose and lignin. Cocoa pods are carbonised and activated using HCl solution to increase the adsorptive power. This research analyzed the influence of adsorbent dose, pH solution, efficiency of hard water reduction and adsorption capacity on Ca^{2+}& Mg^{2+} ions. Adsorbent doses used are 1, 3, 5, 7 & 9g and varying at pH 5, 6, 7, 8 & 9. Study concludes that adsorption capacity increases with increasing pH of the solution and is inversely proportional to dose used. The results showed that AC from cocoa pod shells could adsorb Ca^{2+}& Mg^{2+} ions from hardwater and are affected by the mass and pH of adsorbent. The equilibrium of adsorption process was achievedat the dose of 5g and pH of 9 with an adsorption capacity of Ca^{2+}& Mg^{2+}ions, at values 0.61mg/g and 0.49 mg/g respectively.

2.2.5.2. Application of Activated Charcoal in Oil Purification.

Oil on storage get rancid that increases free fatty acid content and make them unfit for consumption. Continuous heating of oil increases the free fatty acid content (Evika, 2011). The greater the levels of free fatty acid content lower the quality of the cooking oil (Nasir *et al*., 2014).

Continuous use of this used cooking oil is harmful for human health causes cancer and artherosclerosis (Evika, 2011). Activated carbons are widely used in oil purification. The use of AC removes toxins that are naturally present. AC is used for bleaching that removes the colour and refines the oil (Sitorus *et al.*, 2020). Acid value and peroxide values of used cooking oils are also reduced by the application of AC.

Loth Botahala *et al*., (2019) studied on the Determination of Effectiveness Absorption of the Rice Husk and Hazelnut Shell to Purification used Cooking Oil. In this study a comparison of water content and as content are carried out. In this article they determine the absorption capacity of the active charcoal of rice husk and hazelnut shells to purify used cooking oil. Candlenut shell charcoal and rice husk are prepared with temperature of 400˚C for 90minutes and activated for 350˚C for 1hr. Then this activated charcoal was used for purification. For candlenut shell AC water content and ash content are 3.398% and 6.667% and that of rice husk AC are 3.355% and 8.667% respectively. While examining the effectiveness of AC in used cooking oil peroxide values were decreased. There was also a decrease in levels of free fatty acid content and water content in oil. Both candlenut AC and rice husk AC meet the requirements of SNI 06-3730-1995. Adsorption capacity is better for candlenut AC than the AC from rice husk. The amounts of peroxide numbers, free fatty acid content and moisture content of used cooking oil adsorbed by the activated charcoal from the shells is higher than the activated charcoal of rice husk.

Khuzaimah and Eraltia (2020) performed a research on Utilization of Adsorbent Carbon Coconut Shell for Purification of Used Cooling Oil. As the cooling oil is one of the primary commodity people need must meet the required standards. Repeated use at high temperatures creates foul smell and reduces nutritional quality. One method to treat used cooking oil is adsorption with carbon made of coconut shells. This research aimed to reduce the acid value and perocide values of used cooking oil. The acid value was determined using acidimetric and alkalimetric titration method, while peroxide value using iodometric titration method. These two methods were used to analyse samples of fresh cooking oil, used cooking

oil and used cooking oil treated with activated charcoal. The use of activated carbons lowers the acid value by 0.7068 with a percentage of 34.1449 and lowers the free fatty acid content by 0.3314 with a percentage of 37.5066.

Sitorus *et al*., (2020) conducted a study on Coconut oil purification using two different concentrations of activated charcoal. The coconut oil is traditionally processed by heating process and normally is neutralized. In order to obtain standardized quality of oil, its necessary to perform purification to traditionally processed oil. This research purpose was to obtain the most effective concentration of charcoal to increase the clarity of coconut oil as well as to remove the particle non-oil like water and free fatty acids. In this study two kinds of different concentration of AC which was 1% and 1.5%. Indonesian National Standard was used to standardize the quality. To test the quality of the oil several measurements was performed which were moisture clarity level, moisture content and free fatty acids content. As the purification of oil was done to enhance colour and extend the shelf life of oil before consumption. When high concentration of AC was used higher clarity was obtained that is in 1.5% AC clarity level was 97.83T. Maximum water content in oil is 0.2%. Water content reduces by the usage of AC and for 1.5% AC value is 0.016%. The free fatty acid content affects the quality of oil during storage. Maximum free fatty acid content in pure coconut oil is 0.2%. By the application of 1.5% AC free fatty acid content was reduced to 0.006%. Hence from this study higher the concentration of AC used, the higher the adsorption capability of AC.

Miskah *et al*., (2019) conducted a research on Purification of used Cooking Oil Using Activated Carbon Adsorbent from Durian Peel. As repeated use of cooking oil can cause increase in free fatty acid content and peroxide values. This oil being used in our day today lives will cause serious health hazards. Thus this oil must be purified before it is discharged to the environment. In Indonesia durian is a kind of seasonal fruit and AC was produced from its peel. Peel contain high cellulose content about 50-60% and is eligible to be used as carbon adsorbent. Carbonization of peel was done at 500^{o}C lasts for 2hrs and activated using chemical H_2SO_4. This study was carried out with 6 grams of AC and various contact times of 30, 60, 90, 120 and 150 minutes. From the results free fatty acid content get reduced as the contact time increases. The most favourable results obtained after contact time was 0.0637% of free fatty acid, 0.41 meq O_2 /kg of peroxide value and 0.9022 gr/ml of density respectively at 150 minutes contact time.

Indah *et al*., (2003) published an article on Activated Carbon Production From Coconut shell with $(NH_4)HCO_3$ Activator as an Adsorbent in Virgin Coconut Oil Purification. AC was produced using physical and chemical process. This research was done to investigate the effect of soaking concentration of ammonium bicarbonate as the activator to the characteristics of product. This research also studied the application of AC as an adsorbent in virgin coconut oil purification. AC was produced by pyrolysis of coconut shell for 6hrs at temperature of 400^{o}C and chemical activation was done using ammonium bicarbonate solution at various concentration ; 0.5%, 1%, 2% and 2.5% for 24hrs. Physical activation was done in thermal reactor for 2hrs at maximum temperature of 800^{o}C. Produced AC was applied for virgin coconut oil purification and best result was obtained from AC with 2.5% concentration of ammonium bicarbonate. Peroxide values and turbidity of VCO obtained are 1 meq/kg and 1.01 NTU respectively.

Qader (2019) wrote an article on Purification of biodiesel using activated carbons produced from spent tea waste. Waste cooking oils can be converted to biodiesel through base catalysed transesterification. After seperating the glycerol, the crude methyl esters werepurified using activated carbons formed from spent tea waste. Yield and fuel properties of produced biodiesels were compared with those purified by using silica gel and water washing methods. AC from spent tea was produced by heating it in a muffle furnace at 600^{o}C. The surface area of produced adsorbent was analysed using iodine adsorption number and FT-IR spectroscope. The spent tea activated carbon can be regenerated and reused for the same purpose. The results showed better results on purification by AC from spent tea than purified using silica gel and water washing methods.

Nadia *et al*., (2020) published an article on The Effectiveness of activated carbon as adsorbent in the oil purification process fish by- product of the fish caning industry. The fish oil waste from canning has low quality but can be recovered by purification process. Bleaching process is done to improve colour of oil. This study was done to determine the effect of use activated carbon to the effective characteristics and concentration on the fish oil purification by-product of fish canning industry. This research method used completely randomized design (CRD) with five treatments with four replications. The concentration used in this study are of 0%, 2%, 4%, 6% and 8%. The results showed that addition of AC adsorbent in the process of bleaching fish oil showed a highly significant ($p<0.01$) on levels of free fatty acids and significantly different ($p<0.05$) on the peroxide value.

2.2.6. Reactivation or Regeneration

With the continuous application, activated charcoal lose the adsorption capacity. In order to restore this, reactivation is carried out. The reactivation or the regeneration of activated charcoal involves restoring the adsorptive capacity of saturated activated carbon by desorbing adsorbed contaminants on the activated carbon surface shown in Fig. 2.5. nitsri.ac.in.

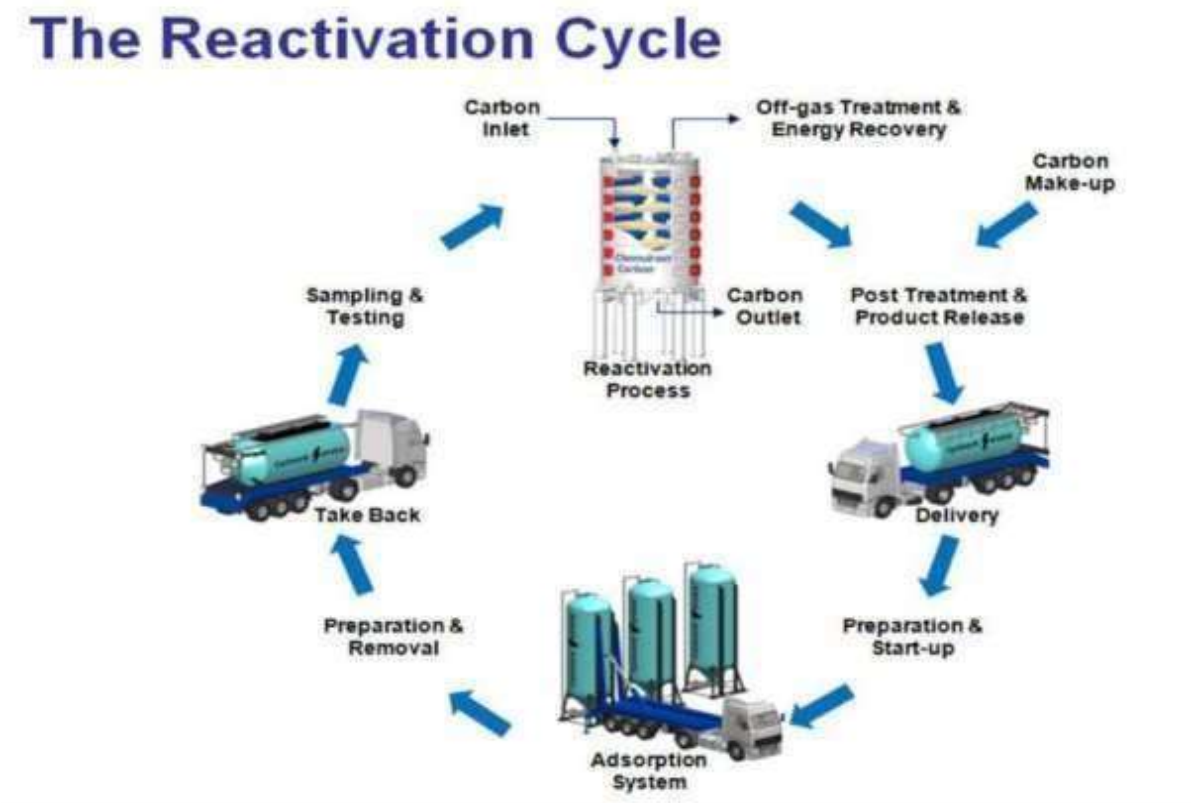

Fig 2.6. Regeneration Cycle.

Source : NTSRI

One of the many advantages to activated carbon is its ability to be reactivated. While not all activated carbons are reactivated, those that are cost savings in that they do not require the purchase of fresh carbon for each use. Regeneration is typically carried out in a rotary kiln and involves the desorption of the components that had previously been adsorbed by the activated carbon. Once desorbed, the once saturated carbon is again considered active and ready to act as an adsorbent.

Thermal reactivation most common regeneration technique employed in industrial processes is thermal reactivation. The thermal regeneration process generally follows three steps: Adsorbent drying at approximately 105°C (221°F), High temperature desorption and decomposition (500 - 900°C (932 - 1652°F)) under an inert atmosphere and Residual organic

gasification by a non-oxidising gas (steam or carbon dioxide) at elevated temperatures (800°C (1470°F)).

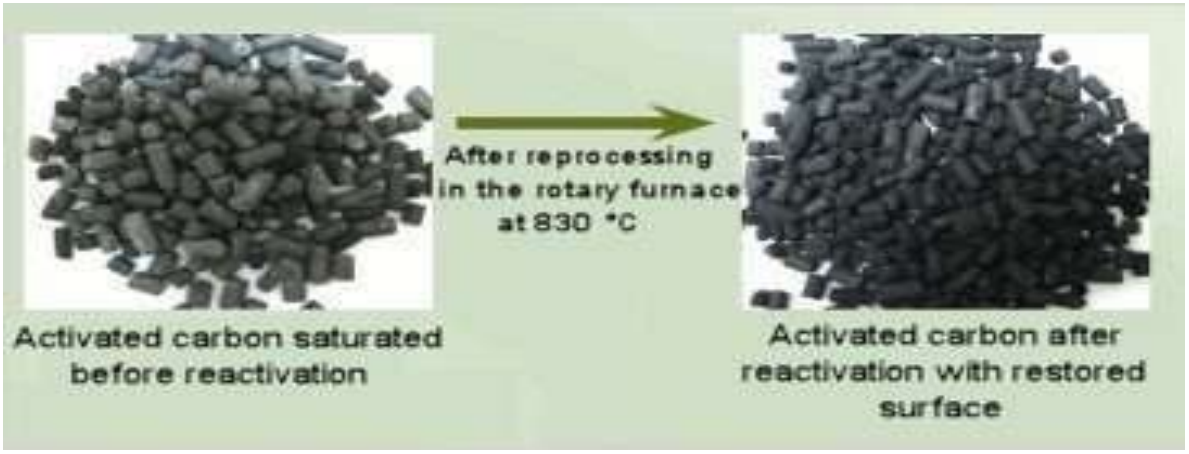

Fig 2.7. Activated Carbon After Reactivation With Restored Surface

Source : NTSRI

Other regeneration techniques are Chemical and solvent regeneration, Microbial regeneration, Electrochemical regeneration, Ultrasonic regeneration and Wet air oxidation.

MATERIALS AND METHODS

CHAPTER - III

MATERIALS AND METHODS

This chapter describes the production and activation of charcoal from cocoa pod. Materials used for the experiment were explained. Various parameters were analyzed for the characterisation of activated charcoal. SEM analysis was also carried out to observe the surface morphology. The adsorption effect of produced activated carbon in the process of water and oil purification was observed.

3.1. RAW MATERIALS

Matured cocoa fruit (*Theobroma cacao L.*) were procured from Cocoa Research Center, KAU, Vellanikara, Thrissur. About 10 Kg of cocoa pod was collected. It was brought to the laboratory and used for sample preparation.

3.1.1. Sample Preparation

Procured cocoa pods were dried under the sunlight for one week to reduce their moisture content from 14% to 7% to produce good activated carbon. Drying also reduces the smoke production during carbonisation. Dried cocoa pods were then weighed, grinded and seived through a mesh size of 150 µm.

Plate 3.1. Dried Cocoa Pod

Plate 3.2. Grinded & Sieved Cocoa Pod

3.2. PRODUCTION OF CHARCOAL

Charcoal is produced by the carbonisation of carbonaceous material in the absence of air. Properties of produced charcoal were also observed.

3.2.1. Carbonisation

Carbonisation was done in a muffle furnace. Muffle Furnace is a laboratory instrument with a maximum temperature of 1000^0C and a working temperature of 900^0C. The sample prepared was placed in the muffle furnace at varying temperature for 1hr. Here time being kept constant and temperature is varied (250^0C, 300^0C, 350^0C & 400^0C) (Table 3.1). The charcoal obtained after the carbonization stage was filtered using a 150 µm sieve to obtainuniform carbon. Charcoal was cooled to room temperature using desiccator (used for cooling heated objects & for the storage of dry objects that must not be exposed to the moisture normally present in the atmosphere). The temperature for carbonisation and sieve size were taken according to reference Ulfah and putra, 2019.

Plate 3.3. Muffle Furnace

Table 3.1. Variations in pyrolysis temperature.

Sample	Temperature
S1	250 ^{o}C
S2	300 ^{o}C
S3	350 ^{o}C
S4	400^{o}C

3.2.2. Characterisation of charcoal

Charcoal produced at various temperatures were analysed. Visual interpretations were done.

3.2.2.1. Ash content

The ash content was determine as per reference ASTM D 2866 -70. According to this Ignite the crucible in the muffle furnace at 600^{o}C for 1 hour. After Placing the crucible in the desiccator. It was cooled to room temperature and weighed to the nearest 0.1 mg. Weigh out to the nearest 0.1 mg, so that the estimated amount of ash will be 0.1 g into the ignited crucible. Place the crucible in the furnace at 600^{o}C. The process will take 2 hours. Place the crucible in desiccator and allow to cool to room temperature. When cool, admit air slowly to avoid loss of ash from the crucible. Weigh to the nearest 0.1 mg.

$$\text{Ash Content (A)} = \frac{(F - G)}{(B - G)} \times 100$$

Where;

B = weight of crucible + original sample

F = weight of crucible + ash sample

G = weight of the crucible

3.2.2.2. Moisture Content

The moisture content of charcoal was determined by using infrared moisture analyser. It is used to measure moisture of any material. The instrument is designed in accordance with the thermogravimetric principle. In the drying process, instrument measures continually and displays immediately the moisture lost (%) from the sample.When the drying is completed, the

finally measured moisture is locked. In the display initial weight, moisture content and measuring time of the sample were displayed.

Plate 3.4. Infrared Moisture Analyzer

3.3. OPTIMIZATION OF CHEMICAL ACTIVATION

Activation was done by soaking 6g of carbon of sieved cocoa pod powder into 25 ml of different activator reagents (HCl, and KOH) with different concentration of 3N, 4 N & 5N (Ulfah and putra, 2019) for 24hrs. Here the chemical used were at various concentration to find the effectiveness. Then these activated carbon were filtered using whatmann filtered paper and washed with aquades until neutral condition obtained. Then heated at 110^{o}C in a cabinet drier for 1 hour to reduce the moisture content and cooled in a desiccator. The AC was optimized by comparing the values with standard specification of activated carbon.

Plate 3.5. Cabinet Dryer

Table 3.2. ASTM Standard specification of AC

Analysis	Quality Requirements	
	Particle	**Powder**
Moisture Content, %	Max. 4.5	Max. 15
Ash content, %	Max. 2.5	Max. 10
Volatile Matter 950 ^{o}C, %	Max. 15	Max. 25
Parts that are not carbonized	0	0
Fixed carbon content	Min 60%	-

Source : Hanum *et al*., (2017) and Ulfah and putra, (2019)

3.4. CHARACTERISATION

Various physio-chemical properties viz. moisture content, ash content, fixed carbon content, pH were analysed .

3.4.1. Moisture Content

The moisture content was determine as per reference ASTM D 2867- 70. The activated carbon was weighed 1 gram and put into a dried crucible silicon, then was heated in the Cabinet drier at 105^{0}C for 1 hour or more until constant weight is gained. Theactivated carbon was then cooled in the desiccator and weighed. Water content can be calculated by the following equation:

$$\text{Moisture Content (M)} = \frac{(B - F)}{(B - G)} \times 100$$

Where;

B = weight of crucible + original sample

F = weight of crucible + dried sample

G = weight of the crucible

3.4.2. Ash content

The ash content was determine as per reference ASTM D 2866 -70. The Activated carbon was weighed 1 gram and put into dried crucible silica, Then it was tarnished into furnace and heated slowly until ashes appeared. The flame of furnace was enhanced up to 600^{0}C and kept it at that temperature for 2 hours. When all the carbon has beenchanged to ashes, cool it

in a desiccator and then weighed to obtain permanent weight.

Ash content can be calculated by the following equation:

$$\text{Ash Content (A)} = \frac{(F - G)}{(B - G)} \times 100$$

Where;

B = weight of crucible + original sample

F = weight of crucible + ash sample

G = weight of the crucible

3.4.3. Volatile Matter Content

The volatile content was determine as per reference ISO 562-1981. The Activated carbon was weighed 1 gram and put into dried crucible silica. It was thenkept at 900^0C for exactly 7 min in muffle furnace. Then the crucible was cooled in a desiccatorand weighed.

$$\text{volatile matter on dry basis (VM)} = \frac{100\,(B - F) - M\,(B - G)}{(B - G)(100 - M)} \times 100$$

Where;

B = weight of crucible + original sample

F = weight of crucible + sample after heating

G = weight of the crucible

M = moisture in percentage

3.4.4. Fixed Carbon Content

The fixed carbon content was determine as per reference ASTM D 3173-16. Fixed carbon content was measured using the equation

Fixed carbon (FC) = 100 – (% moisture content + % volatile matter + % ash content)

3.4.5. Vapor Content Analysis

The vapor content was determine as per reference ASTM D 2867- 70. The activated carbon was weighed 1 gram and put into a dried crucible silicon and keptin the muffle furnace that was heated up to 310˚C and then turn off the furnace. After the temperature of the furnace reached below 100˚C, the activated carbon was removed and then put in to desiccator and cooled. Vapor content can be calculated by the following equation:

$$\text{Vapor Content} = \frac{a - b}{a} \times 100$$

Where:

a =initial activated carbon weight (g)

b = activated charcoal weight after heating (g)

3.4.6. Bounded Carbon Content Analysis

The bounded carbon content was determine as per reference ASTM D 3173-16**.** The bounded carbon content of activated carbon was obtained from the results of thereduction of parts lost on heating 310^0C (vapor content) and ash content.

Pure activated carbon = 100 - (A + B)

Where:

A = ash content (%)

B = vapour content (%)

3.4.7. pH Measurement

pH was determined using the standard method ASTM D 3838 - 80. pH is the negative logarithm of hydrogen-ion concentration in gram per litre. 1g of activated carbon was put in the conical flash and 100 ml distilled water was added to it. The mixture was stirred for 1 hour and filtered to remove particles. pH readings were taken using pH meter after standardization.

Plate 3.6. Digital pH meter

3.4.8. Scanning Electronic Microscope (SEM)

Scanning Electronic Microscope is a type of microscope which is used for visualization of porous structure of a material. It uses a beam of highly energetic electrons to scan a sample and create its image. Electron gun acts as a source for electrons here. The electron beam is focused by a pair of condenser lenses made of magnets. These magnets are capable of bending the path of electrons. Sample was placed in the sample chamber for analysis. The electron beam strike the sample, get decelerated. It produced a variety of signals like secondary electrons, back scattered electrons, diffracted back scattered electrons, photons, visible light

and heat. The secondary electrons were picked up by the detectors and produced the images of the object's surface on the monitor. The entire operation took place inside a vaccum chamber. The activated carbon samples was analysed in a SEM to visualize the porous structure. The magnification was adjusted for getting a clear picture (Annika *et al.*, 2022).

Fig 3.1 SEM set up

Source : NIT-Rourkela

3.5. EFFECT OF PRODUCED ACTIVATED CHARCOAL IN PURIFICATION OF OIL AND WASTE WATER

Activated charcoal has good adsorptive capacity. They adsorb color, odour, chemicals,minerals etc.

3.5.1. Oil purification (To determine the effect of charcoal in reduction of Free fatty acid content)

Fats are usually broken down into free fatty acid and glycerol by lipases. Continuous heating of oil increases the free fatty acid content and make it unfit for consumption. Effect of produced activated carbon in the reduction of free fatty acid in used cooking oil was tested.

Reagents:-

- 0.1N KOH accurately standardised with N/10 potassium hydrogen pthalate. Using pthalate mixing phenophthalein indicator light pink colour as end point.
- **Solvent:** Mix 1L ethanol and 1L diethyl ether in equal proportions. Neutralise sharply before with N/10 sodium hydroxide solution, using phenophthalein as indicator. 1% phenophthalein in alcohol.

Procedure:-

About 5 g of oil is weighed accurately into a 25 ml conical flask to which 25 ml of mixture of equal volume of alcohol and ether added. Add 1 ml of phenophtalein as indicator. This is titrated against N/10 KOH constant shaking until pink colour persist for 15 seconds. Titrate value in ml was noted.

$$\text{Acid Value} = \frac{56.1 \times V \times N}{\text{Weight of oil}}$$

Where;

V = volume of KOH

N = normality of KOH

Free fatty acid content = Acid value / 2

3.5.2. Water Purification (adsorption of colour)

Activated carbon is a good adsorbent. Hence it's effect is analysed in pond water and clay water to adsorb the colour and visual observations in the change in colour were noted.

RESULTS AND DISCUSSIONS

CHAPTER - VI

RESULTS AND DISCUSSIONS

This chapter deals with the results obtained from the experiments conducted in production of AC, characterization of AC and adsorption effectiveness of AC in purification of oil and waste water.

4.1 PRODUCTION OF CHARCOAL

4.1.1. Prepartion of Activated Carbon from Cocoa Pod

The preparation of activated carbon from cacao pod carried out through two stages: carbonization and activation stage. Sample preparation was the first action to carry out this research. The shell of cacao pod (Theobroma cacao L) which has been collected (80% MC) , diced and then cleaned from dirt with water. After washing, the sample from the cocoa pod were dried under the sunlight to reduce the water content of the cocoa pod shells to 14% and was to reduce smoke during the pyrolysis process.

4.1.2. CARBONIZATION OF COCOA POD

4.1.2.1.Temperature Variation

The carbonization stage was a change in the cacao pod shells into carbon. Cacao pod samples were pyrolysed at varies temperature like 250^{o}C, 300^{o}C, 350^{o}C & 400^{o}C for 1 hour. Characterisation of the carbonised product were carried out in terms of water content, ash content, vapor content, bound content, fixed carbon content and volatile content which depict the optimum temperature for charcoal production. The produced charcoal after pyrolysis at different temperature were shown in the following figures (Plate 4.1, 4.2, 4.3 & 4.4).

Plate 4.1. Pyrolysed Carbon @ 250ºC

Plate 4.2. Pyrolysed Carbon @ 300ºC

Plate 4.3. Pyrolysed Carbon @ 350ºC

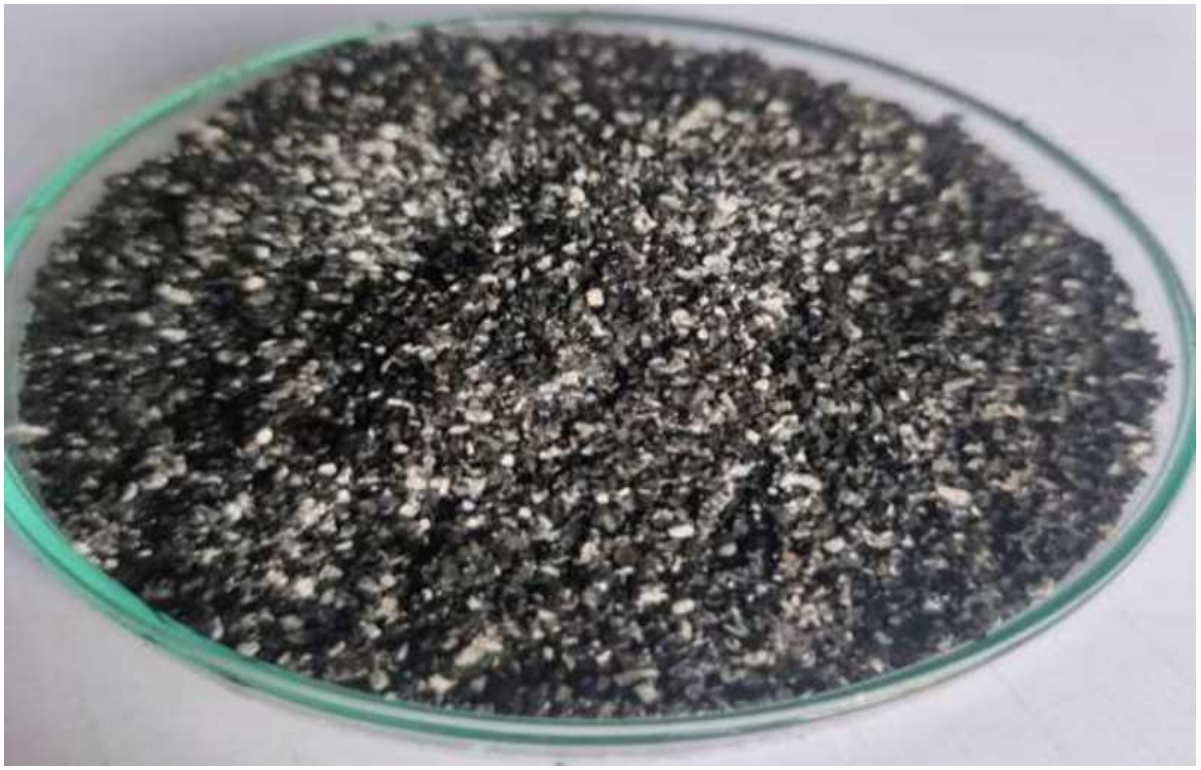

Plate 4.4. Pyrolysed Carbon @ 400ºC

Carbon pyrolyzed at 300^{o}C has an optimum level of moisture content 7.9 % (wb) and ash content of 25%. Particles of sieved sample were uniformly pyrolyzed to get a black, porous carbon at 300^{o}C.

Pyrolysis at 250^{o}C results in nonuniform carbonization of the sample, that would effect the adsorption capacity of charcoal. One-fourth of the sample was reduced to ashes at 350^{o}C and two-fourth of the sample was tarnished to ashes at 450^{o}C pyrolyzes temperature.

From the above results carbon pyrolyzed at 300^{o}C met the requirements of standards for AC and was opted for further process.

4.2. ACTIVATION OF COCOA POD

Pyrolyzed carbon at 300^{O}C was activated using two chemical reagents viz. HCl and KOH. Various concentration of these reagents was used for activation viz. 3N, 4N and 5N. Activation stage converts carbon into activated carbon by producing more pores (Ulfah & Putra (2019).

Plate 4.5. Activation by HCl & KOH at different normalities

4.2.1. CHARACTERIZATION OF ACTIVATED CHARCOAL

The characteristics of activated charcoal were analyzed using two methods:

- Proximate analysis using physio-chemical properties viz. moisture content, ash content, volatile matter content, fixed carbon content, vapor content, bounded carbon content and pH.
- Qualitative analysis in the form of SEM analysis.

The results are discussed in this section. Results obtained were compared with the standards to opt suitable AC.

4.2.1.1. Moisture content

Water content analysis is carried out to determine the content of water remaining in activated carbon after going through the activating process using variations in activator concentrations. As per the ASTM Standard moisture content of particle size AC is max 4.5%. Less MC could increase the adsorption capacity of activated charcoal (Yulisman *et al*., 2017).

Here moisture content increases with the increase in activator concentration. AC obtained by the activation using HCl and KOH at 3N, 4N and 5N has met the requirements of as per the standards shown in Table 4.1. and Fig.4.1. Ulfah and putra, 2019 reported that a water content of 1.59% was obtained using 4N HCl activated carbon.

Table 4.1 Moisture Content of Activated Charcoal

Normality	Reagents	
	HCl	KOH
3N	0.076	0.1
4N	0.0113	0.8241
5N	0.093	0.837

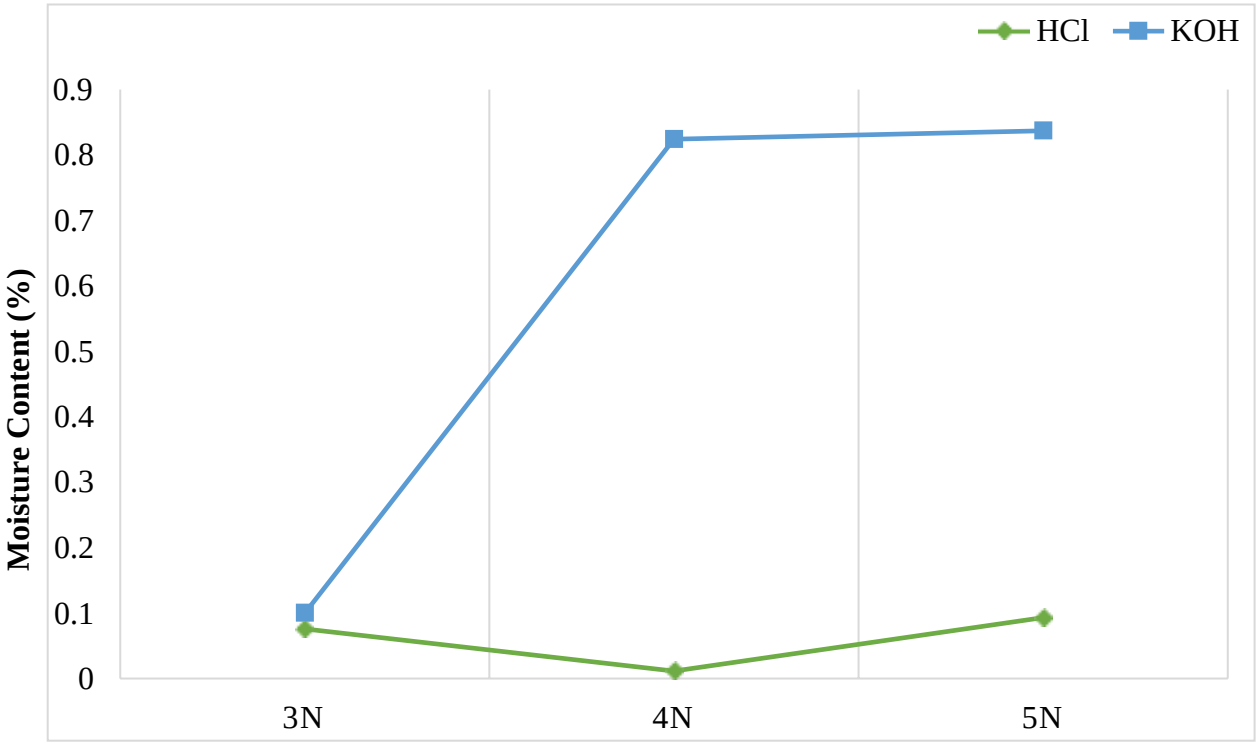

Fig 4.1. Moisture Content analysis of AC with various normality

4.2.1.2. ASH CONTENT

Ash content analysis aimed to determine the metal oxide content that is still present in the AC after going through activating process using variations in activator chemicals concentration (Ulfah and Putra, 2019). Presence of excessive ash can lead to clogging of the pores of AC that will reduce the surface area and the effectiveness of activated charcoal (Yulisman *et al*., 2017).

As per ASTM Standards maximum ash content present in particle size AC is 2.5%. KOH activated AC has high ash content about 10-13% at various normality. AC produced by the HCl activation at 3N shows least ash content about 0.5%. Ash content of activated charcoal made by the HCl activation at 4N and 5N are 1.06 % and 3 %, respectively shown in Fig 4.2. Hence charcoal activated usingHCl at 3N and 4N has met the requirements of the standards. Ulfah and putra 2019 reported that a ash content of 1.19 % was obtained using 4N HCl activated carbon**.**

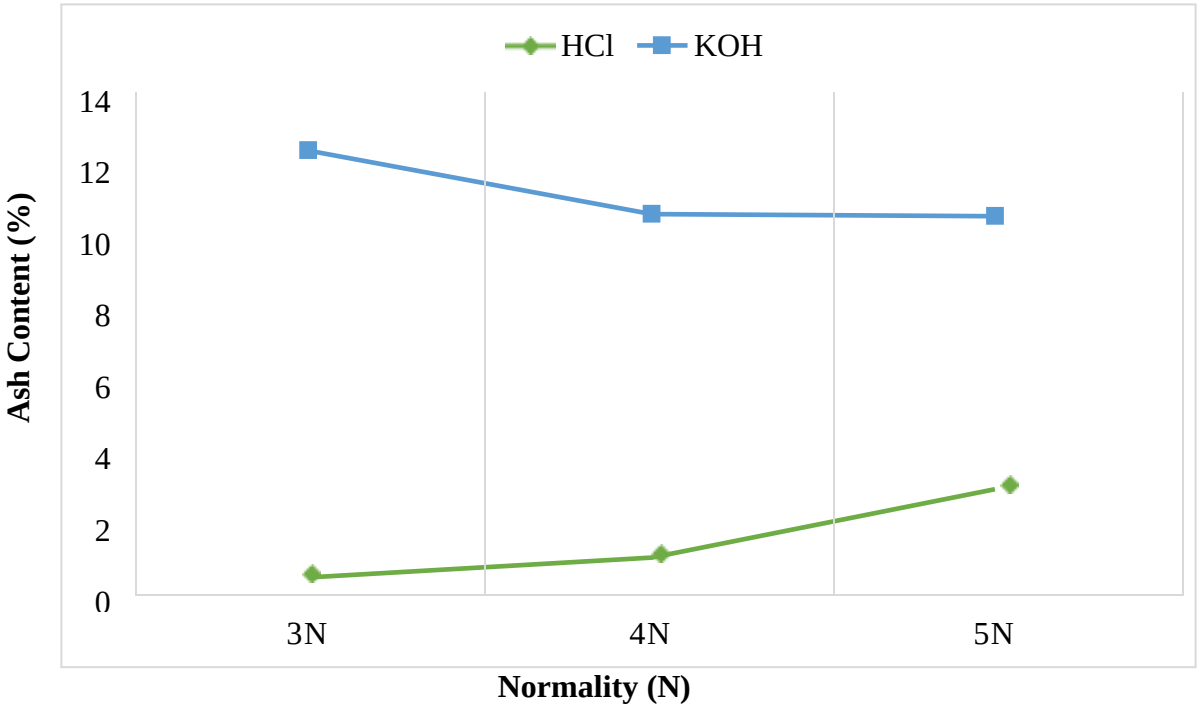

Fig 4.2. Ash Content analysis of AC with various normality

4.2.1.3. VOLATILE MATTER CONTENT

Volatile matter is established using the loss in mass resulting from heating. As per ASTM Standards maximum 15% is the required volatile matter present in particle size activated charcoal. The levels of volatile matter decrease as activator concentration increases (Yulisman *et al*., 2017). AC produced by HCl treatment at 3N, 4N and 5N has volatile matter content of 50%, 40% and35% respectively. Charcoal activated at 3N HCl has only met the specified requirements.

4.2.1.4. FIXED CARBON CONTENT

The fixed carbon content of activated charcoal is inversely proportional to water, ash and volatile matter content. Required fixed carbon content in AC is minimum 60% as per the ASTM Standards. Here fixed carbon content decreases with increase in activator concentration. Decrease in carbon content may be caused by the reaction between the carbon and the activator at high concentrations, which can damage the micropore on the carbon surface. Fixed carbon content is influenced by the contents of lignocellulosic materials viz. lignin and cellulose that could be converted to carbon atoms (Carolina *et al*., 2015). Fixed carbon content of AC activated using HCl by 3N, 4N & 5N are 61.9%, 58.92% & 49.4%, respactively.

4.2.1.5. VAPOR CONTENT

Vapor content analysis aimed to determine the amount of substances that have not evaporated in the carbonization and activation process but evaporate at 310˚C. From the results vapor content decreases as the activator concentration increases. As per the ASTM standards value of vapor content is maximum of 25%. Fig 4.3 shows the vapor content analysis of AC from various concentration at activator reagent HCl with 3N, 4N & 5N.

At 3N Vapor content was 10.2%, at 4N and 5N values obtained are 8.05% and 9.25%, respectively as shown in Fig 4.3. The larger the size of the activated charcoal, the higher the volatile contained in it. Imperfections in the decomposition of noncarbon components such as CO_2, CO & H_2 and the length of activation can result in high levels of volatile in AC (Ramdja *et al*., 2008).

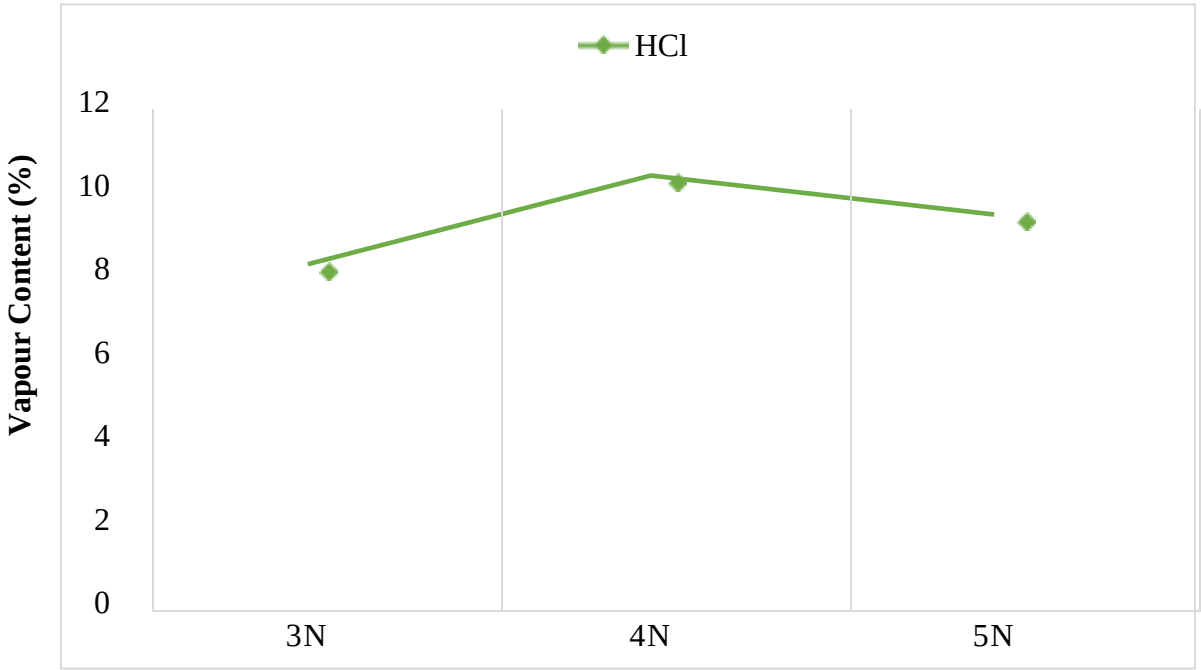

Fig 4.3. Vapour Content analysis of AC with various normality

4.2.1.6. BOUNDED CARBON CONTENT

Bounded carbon content analysis aimed to determine the bounded carbon content after carbonization and activation process Ulfah and putra ,2019. As per ASTM standards bounded carbon content is min 65% in produced AC. Fig 4.4 shows the bounded carbon content analysis of AC. AC activated using 3N HCl shows a result of 90.89%. The results of AC activated by 4N & 5N HCl are 88.03% and 85.7%, respectively.

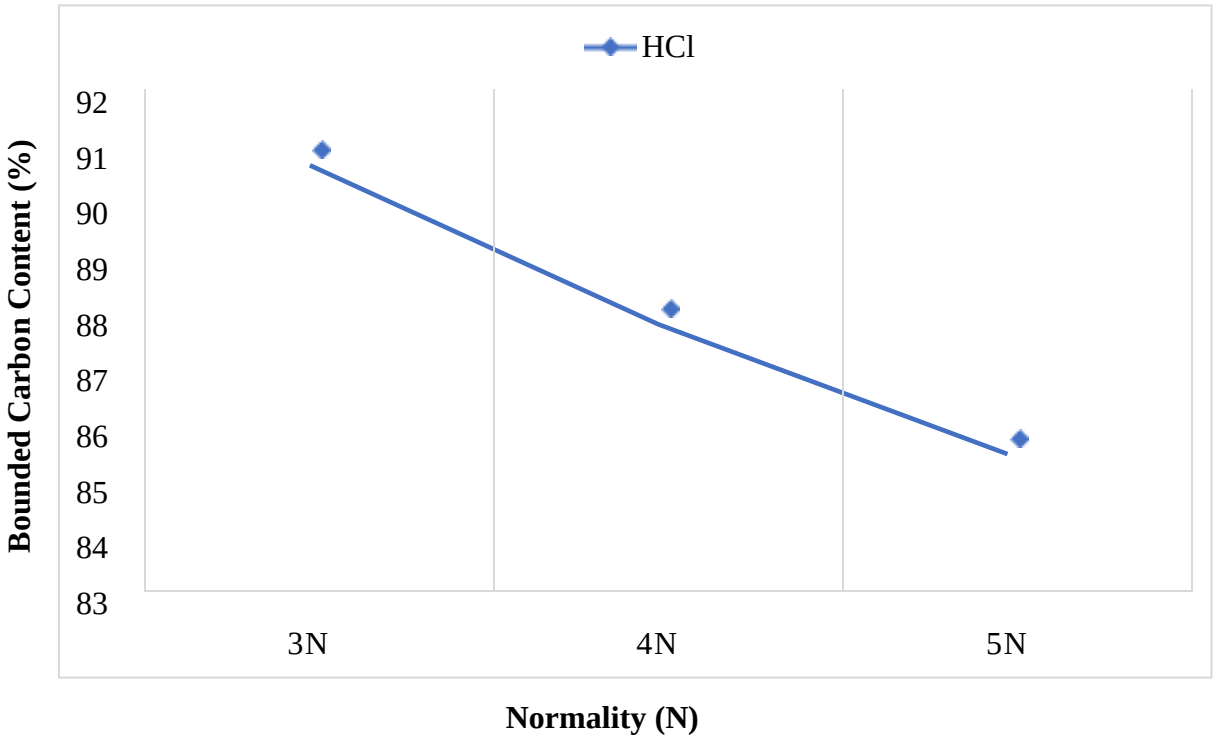

Fig 4.4. Bounded Carbon Content analysis of AC with various normality

4.2.1.7. pH

As per ASTM Standards the pH of activated charcoal is 4 -7. HCl treated sample with various concentrations has met the specified requirements. KOH treated sample has pH ranges from 6-9. By conclusion this may be due to the inadequate washing after activation.

4.2.1.8. Scanning Electronic Microscope (SEM) Analysis

SEM analysis is used to visualize the surface morphology of the product that has been carbonized and activated. Surface characteristics of AC has pores and cavity distribution on its surface. Pores are formed from evaporation and breakdown of non-carbon compounds contained in the sample. The presence of activator enlarged the pores of AC and expanded the surface (Annika *et al.*, 2022).

SEM images were taken to observe the surface topography of the sample. Basically the pore structures of AC were observed. The micrographs of AC are shown in Fig 4.5. AC produced by 3N HCl activation has pore size ranges from 10 – 11 µm. AC produced from 4N & 5N HCl has pore size ranging from 3 – 8µm. Adsorption effect increases as the pore size increases.

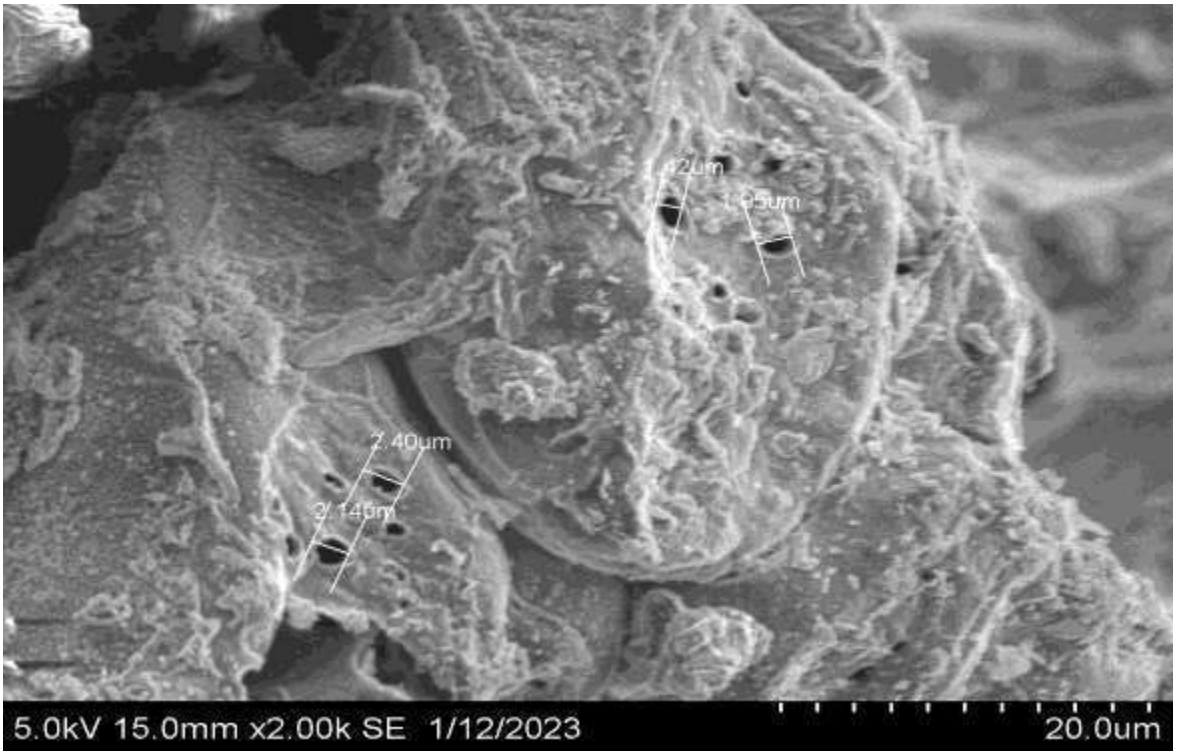

Fig 4.5 a- SEM Image of Untreated Charcoal

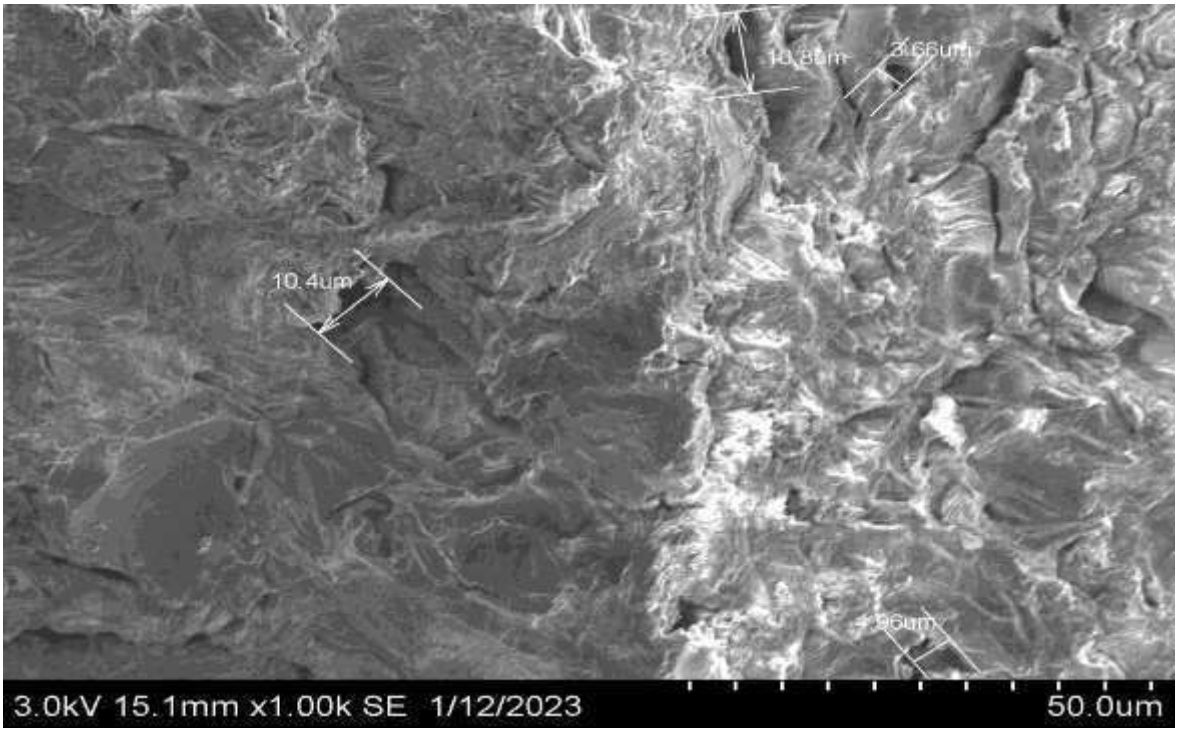

Fig 4.5 – b SEM Image of AC Treated with 3N HCl

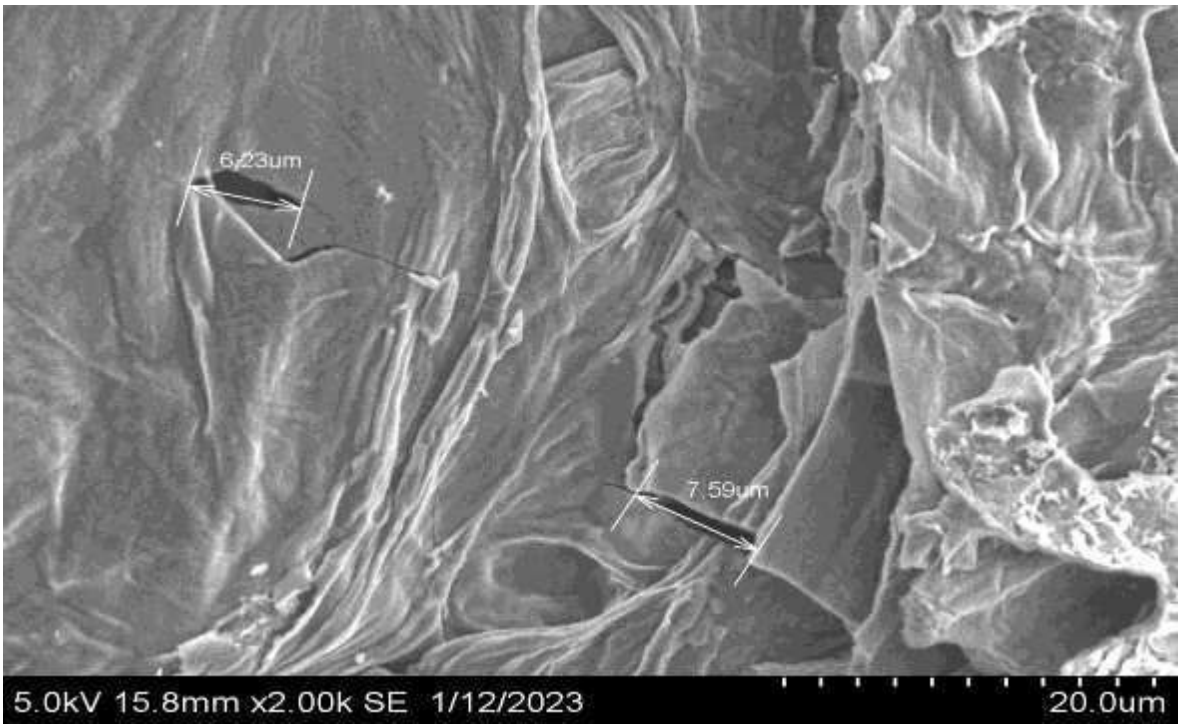

Fig 4.5 – c SEM Image of AC Treated with 4N HCl

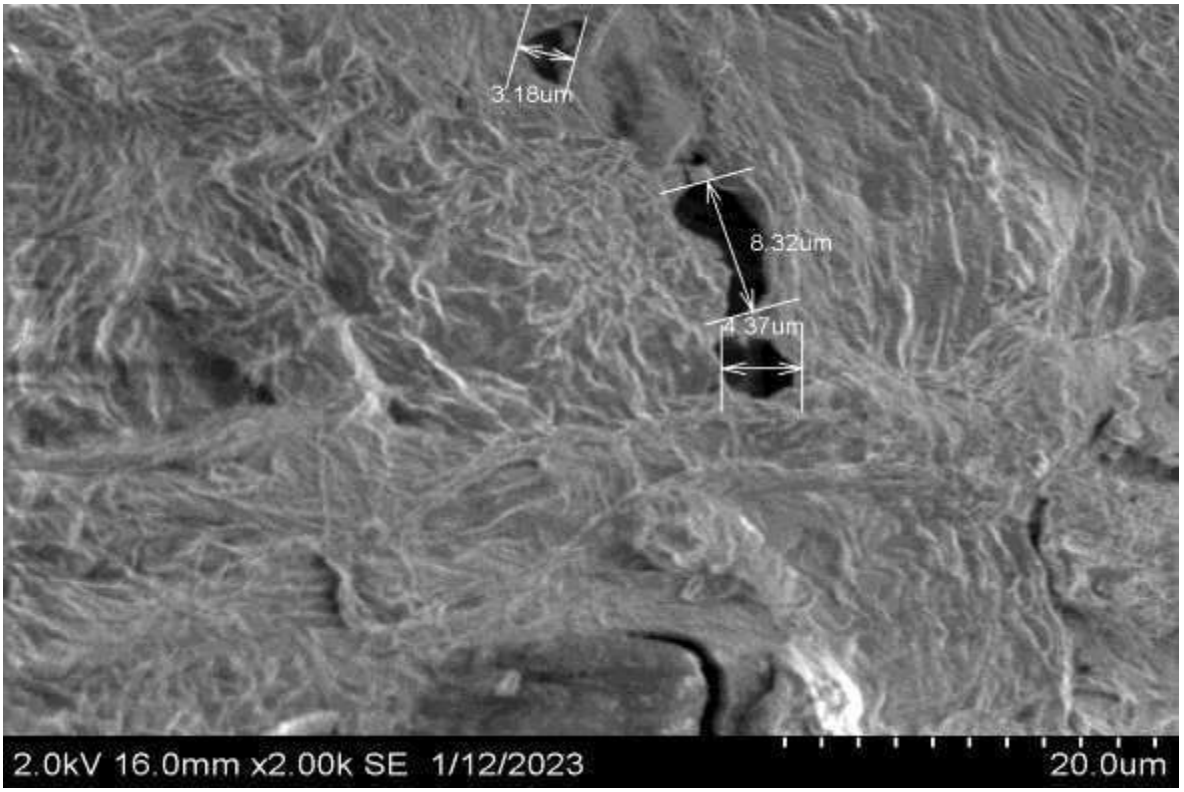

Fig 4.5 – d SEM Image of AC Treated with 5N HCl

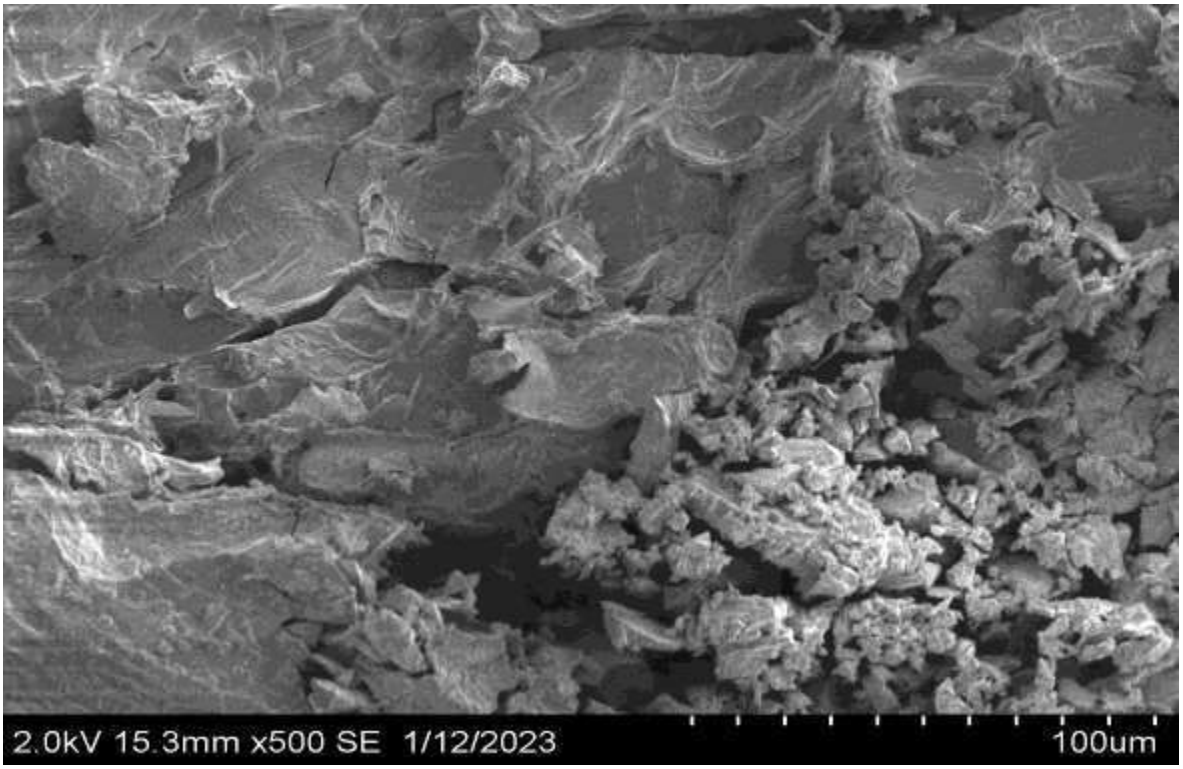

Fig 4.5 - e SEM Image of AC Treated with KOH

From the above observations, AC produced by the chemical activation using KOH has been rejected. One of the steps involved in activation process was washing. Washing of AC produced using KOH requires large amount of water and was time consuming.

From the above characterization parameters, activated charcoal produced by the chemical activation of HCl with 3N has met all the specified requirements as per the standards. AC produced has a moisture content (0.076%), ash content (0.5%), volatile matter content (50 %), fixed carbon content (61.9%), vapor content (10.2%) & bounded carbon content (90.89%), respectively. SEM analysis showed that pore size increased from 2µm in untreated charcoal to 10 - 11µm in 3N, HCl treated charcoal (observed from SEM Images).

4.3. EFFECT OF AC IN OIL PURIFICATION

Standard limit of free fatty acid content in edible oil is ≤0.05%. In used cooking oil the free fatty acid content exceeds 2%, that are discarded. Data from the results of testing of free fatty acids on used cooking oil before and after purification using activated charcoal are 2.57 to 1.18. The results showed that there was a slight decrease in free fatty acid content in used cooking oil.

4.4. EFFECT OF ACTIVATED CHARCOAL IN WATER PURIFICATION.

Results of purification of pond water and clay water showed positive feedback through visual interpretation. Activated charcoal prepared from 3N HCl was placed in water with a contact period of 24 hours. Slight greenish color in pond water due to the algal presence was turned to colorless on addition of AC. In clay water, AC adsorbed the colour and helped the particles to sediment shown in Fig 4.6.

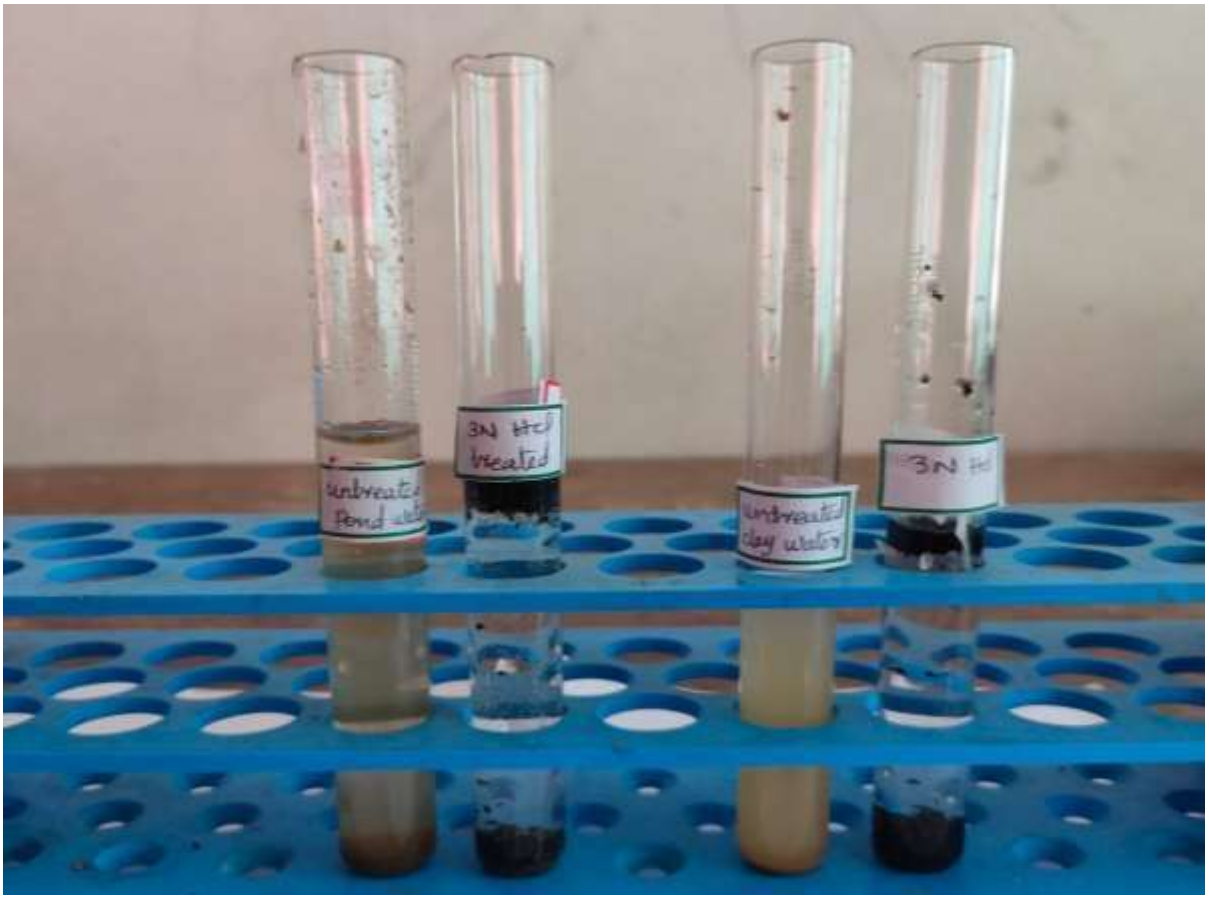

Fig 4.6 Sample for Water Purification

CONCLUSION

CHAPTER V

SUMMARY CONCLUSION

Theobroma cacao L. widely known as cocoa is major cash crop cultivated across the world.the plant was consumed by human as early as 5000 years ago.On an average a fruit is 180 – 200 mm long and weighs about 400 to 500g.Criollo, forastero, trinitario are the major cocoa varieties. The cocoa fruit consists of three main components, viz., pod, placenta and bean. The pod is the largest part of the cocoa fruit and occupies more than 70% of the weight of the ripe cocoa fruit. The percentage of cocoa beans is about 27-29%, the remainder being the placenta that connects 30- 40 beans.

Cocoa beans from cocoa is the main raw material in the production of chocolates, cosmetics, health drinks etc. Cocoa butter is also used in the production of pharmaceutical products (Opeke, 1987). The cocoa bean powder is the raw material for the preparation of chocolates, ice-cream, soft drinks and confectionaries. But cocoa pod still being the largest part and occupying 70% of the cocoa fruit is wasted simply causing extensive pollution to the environment. Cocoa pod contain 51.98% lignin, 21.06% hemicellulose, 20.15% cellulose, 6% pectin, 0.15-0.4% theobromine. It cannot be used as animal feed because lignin is indigestible in animals.

In this study, we have converted cocoa pod into activated charcoal that has wide range of application in numerous industries. It was done in two stages, carbonisation and activation. Dried cocoa pods were weighed, grinded and seived through a mesh size of 150 µm. Cocoa pod powder was pyrolysed at 250^0C, 300^0C, 350^0C & 400^0C in muffle furnace for 1 hr. Activation can be either physical or chemical activation. We prefered chemical activation because it has advantages like good porosity, higher yield and less activation time and energy then physical activation. Activation was done by soaking 6 grams of carbon of sieved cocoa pods into 25 ml of different activator reagents (HCl & KOH) with different concentration of 3N, 4 N and 5N for 24 hours. Here the chemical used are at various concentration to find the effectiveness.

Then these activated carbon were filtered using whatmann filtered paper and washed with aquades until neutral condition was obtained. It was then heated at 110^oC in a cabinet drier for 1 hour to reduce the moisture content and cooled in a desiccator to obtain the final product. Various parameters were analyzed for the characterisation of activated charcoal. SEM was also

anlysed to observe the surface morphology. The adsorption effect of produced activated carbon in water and oil purification was observed.

The optimum temperature for making carbon pyrolysis process was 300ºC for 1hour. Pyrolysis at 250ºC resulted in non-uniform carbonization of the sample, that would effect the adsorption capacity of charcoal and samples were converted to ashes in pyrolysis at 350ºC and 450ºC. HCl at 3N was the better activating reagent with moisture content (0.076%), ash content (0.5%), volatile matter content (50 %), fixed carbon content (61.9%), vapor content (10.2%) & bounded carbon content (90.89%), respectively.chemical activation of HCl with 3N has met all the specified requirements as per the standards. There was an increase in pore size from 2µm to11µm on SEM analysis. The produced activated carbon was able to clarify water and adsorb free fatty acid content in oil effectively.

From this study, we could say that activated charcoal from cocoa pod can play a great role in the reduction of environment pollution. Millions of chocolates are produced each year around the world, and cocoa pod which is a major by-product can be used efficiently converting it to activated charcoal.

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ABSTRACT

PRODUCTION AND CHARACTERIZATION OF ACTIVATED CHARCOAL FROM COCOA POD

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ABSTRACT

Cocoa *(Theobroma cacao L.)* is one of the widely cultivated crops in the world. Cocoa fruit consist of cocoa pod (70%), cocoa bean (27-29%), and placenta (1-3%). cocoa bean is the major raw material in the production of chocolates, ice-cream, soft drinks, confectionaries, cosmetics, health drinks, and pharmaceutical. But cocoa pod being the major by-product is wasted causing extensive pollution to environment. Cocoa pod can be converted to activated charcoal that has wide range of application in various industries.in this study activated charcoal was prepared from cocoa pod.

The production of AC was done in two stages. First carbonization of cocoa pod by pyrolysis to produce charcoal, then activation of produced charcoal using chemicals to increase its porosity. The process parameters were pyrolysis temperature (250ºC, 300ºC, 350ºC, 400ºC) chemicals used for activation (HCl & KOH) and normality of chemicals used (3N, 4N, 5N). The optimized condition was found to be pyrolysis at 300ºC for 1 hour with HCl as best activating reagent at a 3N. The activated charcoal obtained using optimised parameters are further characterised by factors such as moisture content, ash content, fixed carbon content, volatile matter content, pH, bounded carbon content and SEM analysis. Finally the produced activated carbon was tested in water and oil to study its effects.