

A Thesis on

**PREPARATION AND CHARACTERIZATION OF ACTIVATED  
CARBON FROM WASTE FOOD PACKAGING POLYMERS**

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**Master of Technology (5 year Integrated Dual Degree Course)**

in

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by

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### **CERTIFICATE**

This is to certify that the thesis entitled, “**PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM WASTE FOOD PACKAGING POLYMER AND ITS APPLICATION**” submitted by **R.SHASHANK.V.RAMAN**, bearing Roll No. - **710CH1115**, in partial fulfilment for his requirements for the award of **Master of Technology (5 year Integrated Dual Degree course)** in **Chemical Engineering at National Institute of Technology, Rourkela** is original work carried out under my supervision and guidance.

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## **ABSTRACT**

The two of the major challenges which we are facing in the modern era are the management of the waste plastics and the waste water from the industries. Water pollution is one of the major challenges faced by the environmental engineers today due to toxic metal releases from various industries. Among various technologies, adsorptive removal of these toxins by the usage of activated carbon as the adsorbent is more promising and economical as it is known for its high adsorption capacity. The preparation of activated carbon from waste food packaging polymers, which is about 35% of the total plastic waste accumulated, would not only reduce the voluminous quantities of plastic but also help in water treatment.

A relatively new technique, Hydrothermal Carbonization (HTC), was used for the carbonization of the raw material instead of the traditional carbonization process. A pressure vessel was fabricated for HTC and the temperature set at 235°C and the holding time was 15 hours. After processing the 'hydrochar' with benzene to remove ash, dirt and iron rust (if there) it was activated with 1 M KOH for a period of 10 hours and subsequent drying for 5 days under the temperature 70°C. Proximate analysis, Field Emission Scanning Electron Microscope (FESEM), Iodine Number, and Methylene Blue Number were the characterization techniques implemented. It was observed that the methylene blue number was high indicating the presence of high percentage of mesopores content.

Keyword: Plastic, Hydrothermal Carbonization, hydrochar.

# **CHAPTER 1**

## **INTRODUCTION**

## 1.0 INTRODUCTION:

Plastic waste accumulation is one of the major environmental and health problems in our country, particularly in the urbanized regions. Plastic bags are one of the main sources of plastic waste in our country. Plastic bags of all sizes, shapes and colours pollute the city's landscape due to the problems of misusing, overusing and littering. Besides this visual pollution, plastic wastes also contribute to the blockage of drains and are a threat to the life in water, and can cause livestock deaths if the livestock consumes these toxins. Furthermore, when they are filled with water from rain, plastic bags breed mosquitoes, which cause malaria and other potentially life-threatening diseases. Also, plastics take many years (20-1000) to degrade and hence pose a challenge of disposal and it is due to this reason that this attempt is being continuously made by many researchers to carry out more research on this problem so that an effective solution may be found out.

### 1.1 Role of Activated Carbon:

One of the methods of controlling the plastic pollution is by using it as alternative source of fuel or by processing it to produce activated carbon. Activated Carbon is one of the important and fast growing cleansing agents which are being used widely in many industries to treat waste water for various hazardous metal ions and organic liquids and also in the incineration and recycling industries to trap the noxious gases which are evolved during the process.

Activated carbons have high microporous and mesoporous structures having medium to high internal surface areas. Cheap sources with high amount of carbon content, low inorganic content could be used as raw materials for preparing activated carbon ([Bansal et al., 1988](#)).

The medium to high adsorption capacity of activated carbon is related to the properties such as internal surface area, volume of the pore and size distribution of the pore. These unique characteristics depend on the type of raw material which has been used for the preparation of

the activated carbon and the activation method. Literature surveys indicated that there have been many experiments carried out in order to obtain cost effective activated carbons from agricultural wastes such as coconut shells, coffee industry wastes, ([Azevedo et al., 2007](#); [Hu and Srinivasan, 2001](#)), wood, ([Gomez-Serrano et al., 2005](#); [Klijanienko et al., 2008](#); [Zuo et al., 2009](#)), cotton stalk, ([Deng et al., 2010](#)), almond shells, ([Bansode et al., 2003](#)), rice husk, ([Fierro et al.2010](#); [Guo and Rockstraw, 2007](#)), date pits, ([Girgis and El-Hendawy, 2002](#)), nut shells, ([Lua et al., 2005](#); [Yang and Lua, 2006](#)).

Keeping in vision, the ever increasing demand of activated carbon, a dire necessity for the sorting out of new raw materials for the preparation of activated carbon, which should be cost effective at par with the commercially available activated carbon. Though, the usage of agricultural wastes as the pre-cursor for the preparation of activated carbon has incremented considerably in recent years, the utilization of waste accumulated plastic materials still has low utilization due to the toxins it itself releases when carbonized. But now, after the introduction of Hydrothermal Carbonization, the utilization is looking at a rise.

## 1.2 Hexavalent Chromium ion [Cr (VI)]:

The activated carbon efficiency with the help of various chemical activations in the reduction of hexavalent chromium [Cr (VI)] to levels below its allowable limit in drinkable water is one of the major research studies in the areas where the metal ore is being extracted. Chromium is normally found in the industrial effluents of the industries such as electroplating, leather tanning and textiles. Cr (VI) appears as the most stable species due to the aerobic conditions in the environment. The trivalent form is not considered toxic but hexavalent chromium affects biological systems and the environment in a severely adverse manner ([Passow et al., 1961](#)), for example exposure to hexavalent chromium beyond the tolerable level of 0.05 mg/L or 5 parts per million (ppm) can have effects of superlative degrees on the human

physiological, biological and nervous systems. Several methods have been adopted for removing Cr (VI) from the aqueous phase ([Agarwal et al., 2006](#); [Baek et al., 2007](#); [Dragan et al., 2004](#); [Kyzas et al., 2009](#)) which includes reduction by chemical processes and precipitation, ionic exchanges, evaporation, crystallization and concentration, electrolysis and electroplating, and the one which is gaining popularity these days due to the cost factor and the high adsorption capacity, carbon adsorption. Removal of pollutants by activated carbon is found to be quite effective, particularly in removing toxic metal ions at various concentrations in order to bring the concentration below the tolerable limits.

### 1.3 Motivation:

Rampant urbanization has caused an increase in the problem of drinkable water shortage as well as the demand for water which is toxin free and could be utilized for daily use. Such a dire situation of chromium contamination of high orders in water is faced by the residents of Sukinda area in Jajpur district of Orissa, India. It has been included in the list of world's top ten polluted places, a survey carried out by Black Smith Institute, New York. It contains about 97 % of chromite ore deposits of India alone and is one of the biggest open cast chromite ore mines on the planet.

Water effluents, which remain untreated, are discharged into the water body from the mines. About more than 60 % of the so called drinkable water contains hexavalent chromium levels which is higher than the twice of the national and international standards (0.05 mg/L) and levels which are over twenty times the standard levels of hexavalent chromium in drinkable water have also been recorded. The only water source for the residents is the Brahmani River but facilities for the treatment of its waters are alluringly scarce. The state pollution control board has seconded the fact that the water quality at various locations suffers from extreme levels of contamination.

#### 1.4 Objectives:

The main objective of the current work is to prepare activated carbon from food packaging polymers for the efficient removal of toxins from industrial wastes.

The specific objectives are:

- Preparation of the activated carbon from waste food packaging polymer by effective activation with 1 M KOH.
- Fabrication of a pressure vessel for carrying out the Hydrothermal Carbonization (HTC) process.
- Characterization of the activated carbon prepared.

# **CHAPTER 2**

## **LITERATURE REVIEW**

## 2.0 LITERATURE REVIEW:

### 2.1 Background:

Plastics have taken the form of critical materials in the modern economic scenario; the annual volume of steel produced is less than that of the volume of plastics. The annual consumption of the world in case of plastic materials has escalated sharply from around 5 million tonnes in the 1950s to nearly 100 million tonnes today. The plastics life cycle involves chiefly 3 stages: manufacturing, usage, and recycling and/or disposal. The usage of plastics ranges from toys to hosepipes, from soft drink bottles to refrigerators, from radio sets to television sets.

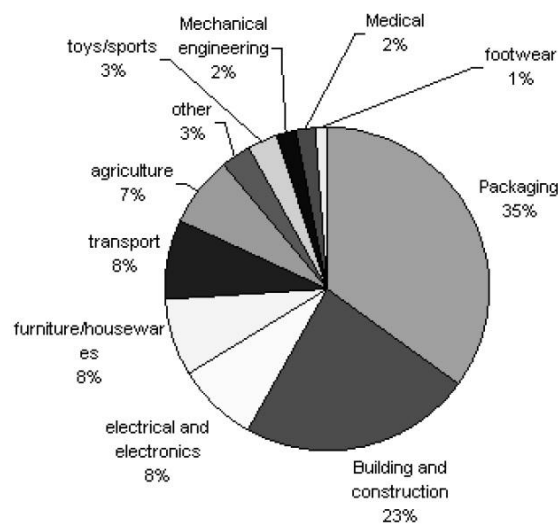


Figure 1: Sector wise usage of Plastic

The plastic recycling is not always green. It usually results in the down cycling of plastics into poorer quality of products that have higher levels of toxic additives which may be present in the form of stabilizers. The inadequate combustion of polyethylene (PE) during recycling causes emission of toxic carbon monoxide. A recycling plant produces the largest effluent amounts during the cleaning and washing processes which also produces waste water. The pollutants which emerge in the disposal stage are mainly produced during incineration or when the wastes fail to reach landfills or incinerators. Given the limited

recyclability of plastics, large amounts of plastic wastes are being burnt in the incinerators which if ineffective in functioning cause the emission of high levels of carcinogens.

## 2.2 Previous work:

Even in the villages in India, plastic and other portions of the waste stream are frequently burned in "back-yard" fires. But the burning of these chlorine-containing substances releases toxic heavy metals and emits noxious gasses like dioxins and furans which cause health hazards. The Indian plastic industry is undergoing growth at a rate of about 17%, with the total consumption of plastics being about four million tons per annum. India is reported to have a relatively high plastic recycling rate of 60% as compared to the world average of 20%. With proper up scaling and standard designing of the autoclave for the HTC process and adequate activation of the char, the activated carbon prepared commercially from the food packaging polymers would not only reduce the volume of the mammoth sized piles of waste plastic without producing any pollution but also could be used for waste water management.

Activated carbon (AC) could be termed as a non-graphitic, non-graphitizable carbon with highly disordered microstructure. Activation of the char could be done in two ways, namely, chemical and physical activation. Chemical activation has various advantages over physical activation. Some of the advantages are:

- Lower activation temperature than the physical activation temperature (800°C-1100°C), ([El-Hendawy et al., 2008](#)).
- It involves a single activation step.
- The yield is higher.
- The porous characteristics are better.
- The time of activation required is shorter ([Nowicki et al. 2006](#)).

The activation agent used in the current work is potassium hydroxide (KOH).

Officially adopted pore classification in respect of the pore size is given in table 1.

Table 1: Classification of pores according to their width ([IUPAC, 1972](#))

Type of pore	Width (nm)
Micropores	(< 2)
Mesopores	(2-50)
Macropores	(> 50)

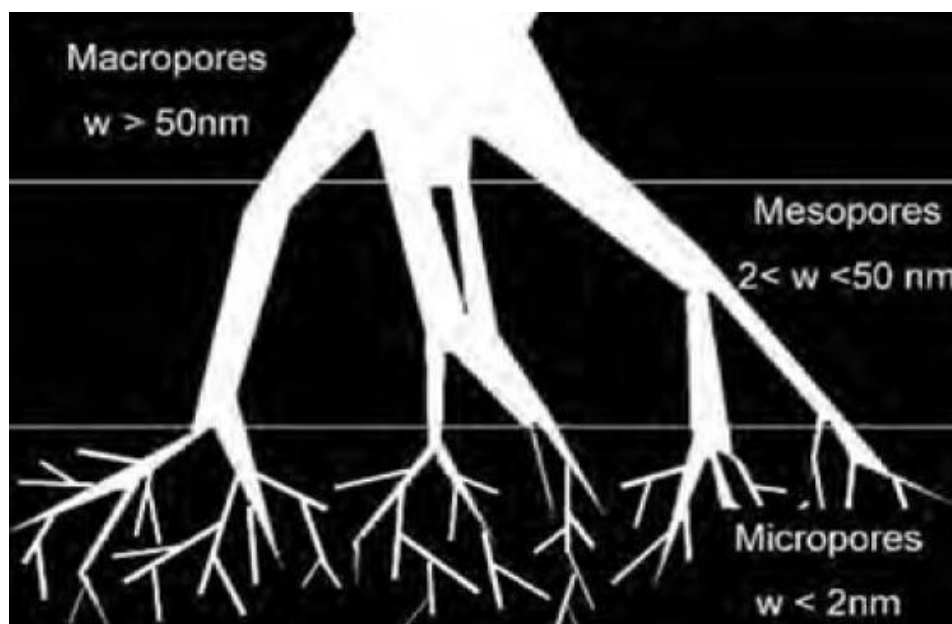


Figure 2: Classification of pores (size)

When the effective radii being less than 2 nm that is the adsorptive action occurs in the micropores, it occurs through the volume filling with no capillary condensation. Generally micropores pore volume is of the order 0.15 to 0.70cm<sup>3</sup>/g, and constitute about 95% of the total Activated Carbon surface area. Generally, the adsorbent microporous structure is characterized by gases and vapours adsorption, and to a minor extent, by small angle X-ray

techniques (Rosas et al., 2009; Zuo et al., 2009; Castro-Muniz et al., 2011; Yang and Lua, 2006; Liou, 2010).

Mesopores, which are also coined as transitional pores, range from 2 to 50 nm of effective diameter. The mesopores surface area constitutes not more than 5% of total surface area and their volume vary between the range of 0.1 to 0.2 cm<sup>3</sup>/g. However, by using special methods, it is possible to enhance mesopores attaining a volume of 0.2 to 0.65 cm<sup>3</sup>/g and surface area of 200 m<sup>2</sup>/g. The characteristics of mesopores include Capillary condensation and adsorption desorption hysteresis (Aworn et al., 2008; Lei et al., 2006; Iang et al., 2010; Hao et al., 2011).

Beside their own the adsorption of the contaminants (say), mesopores also act as conduits leading to the adsorption of the contaminants to the micropore network. In generic terms, the mesopores are characterized by electron microscopy (Liou, 2010; Zhu et al., 2007; Hu and Srinivasan, 2001; Kennedy et al., 2007). Enhanced mesopores percentage attains volume of 0.2 to 0.65 cm<sup>3</sup>/g and surface area of 200 m<sup>2</sup>/g. Pores which have effective radii larger than 50 nm are termed as macropores, which fall in the range 500 to 2000 nm but the contribution in the adsorption is very small and it doesn't exceed 0.5 m<sup>2</sup>/g and 0.2 to 0.4 cm<sup>3</sup>/g respectively. Hence, macropores are not of considerable importance in the adsorption process but they can act as transport channels for the contaminants into the micropores and mesopores networks.

In the work of (Poerschmann et al., 2014), Poly (vinyl chloride) (PVC) was subjected to hydrothermal carbonization in subcritical water from the temperature ranging from 180 to 260 °C. Dehydrochlorination of the raw material taken had increased with increasing reaction temperature. The results provided strong evidence that hydrothermal carbonization discarded PVC-plastic residues are environmentally safe regarding the formation of toxic organic products. Following the discussions and the inferences of the work, hydrothermal treatment of PVC-waste at and beyond operating temperatures of 235 °C to allow complete release of organic chlorine should be further pursued.

Carbonization of plastic can't be carried out in the traditional manner since its heating to elevated temperatures releases toxic aromatic gases as mentioned in the introduction. Thus, hydrothermal carbonization process is used to contain the toxic gases which evolve during the carbonization as the toxic gases get dissolved in water present.

Application of activated carbon:

Activated carbon is a brilliant adsorbent whose properties are versatile and its main applications include the adsorptive removal of colour, odour, taste, and other undesirable organic and inorganic impurities from drinkable waters; in the industrial waste water treatment; purification of air; in food processing; in the chemical purification, in pharmaceutical product productions; respirators used in hostile environments works; and in a various other applications of gas-phase. Nearly 80% of the total activated carbon produced is being consumed in applications in liquid phase ([Moreno-Castilla and Rivera-Utrilla, 2001](#)).

The aqueous phase adsorption for the removal of both organic and inorganic compounds has been a very important application of activated carbon and researchers have reported potential applications of granular activated carbons to liquid phase contaminant removals. By using activated carbon, results obtained were at par with the expected results and in the removal of organic chemicals from water ([Gupta et al., 2006](#); [Jarvie et al., 2005](#)) and the adsorptive removal of organic compounds was compared with the inorganic ones ([Moreno-Castilla, 2004](#)). Among the inorganic pollutants, heavy metal ions stand out due to their persistence and toxic nature. The influx of heavy metal into ground water and surface water has been on an increase due to the unimplemented restrictions in industrial processes for waste water purification. Various heavy metals which arise commonly due to mining and discharges from the industries have been found to be contaminating the waters of the nearest water body. According to World Health Organization ([WHO, 2004; 2006](#)), the heavy metals of the highest toxicity include cadmium, chromium, copper, lead, mercury, and nickel.

The alternative sources for the derivation of activated carbon as the industrial carbon which are available in the market are quite expensive. The attempts of preparation of AC by recycling different types of waste materials and its application in various aqueous-phase treatments which have been made so far to find activated carbon precursor in waste materials has been deeply explored. The precursors have been divided into 2 categories which are non-conventional (from municipal and industrial activities) and conventional (from agriculture and wood industry) wastes that can be applied in various aqueous treatment processes namely to organic pollutants, dyes, volatile organic compounds and heavy metals. A tough competition could be given to the commercial ACs if the activation (physical or chemical) could maximize the surface area and the capacity of adsorption.

Out of the numerous precursors some are Vineyard shoot, Cassava peel, Olive pit, olive cake, date pit, Walnut shell, coffee bean husk, corn cob, cedar wood, teak sawdust, fir wood, pinewood sawdust, oak wood, chestnut, coast live oak wood, cedar wood tropical tree wood, rubber wood sawdust, eucalypt sawdust, mahogany sawdust, pine wood, and cherry stone. And the activating agents for the similar sequence are phosphoric acid, potassium hydroxide, zinc chloride, carbon-dioxide, and steam. The contaminants which were removed by the prepared ACs were dye (methylene blue), dye (malachite green), dye (acid yellow, acid blue), dye (acid blue 80), melanoidin (brown polymer), VOC, metal ions, organics, herbicides and heavy metals. The non-conventional precursors which have been discussed in the work are PET (plastics), coal tar pitch, sago waste, furfural residue (chemical) buffing dust (leather industries), tires, sewage sludge and fertilizers. The various contaminants which have been recorded to be removed are methylene blue, phenol aniline, 2,3,4 trichlorophenol, dye (rhodamine-B), mercury (II), heavy metals, copper ions, mercury (0), anionic dyes, dye (saphranine) in the same sequence as the precursors.

The work concludes with the following points:

- 1) With both conventional types of raw materials (agriculture and woody wastes), AC with high surface areas might be obtained and adsorption behaviour might be controlled by carefully manipulating preparation parameters. AC can give a strong competition with the commercially prepared activated carbon, some of them presenting even better behaviour.
- 2) The physical activation of the char is being widely used. The activated carbon might even be utilized as a catalyst support and also for the removal of contaminants such as organic compounds, dyes and heavy metals (namely chromium and copper).
- 3) The activated carbon, in general, shows good texture and the adsorption mechanism was, majorly, dependent on the pH of the solution.
- 4) The activated carbon has the potential to compete with the commercial ACs.

Study on the comparison of the composition, the structure and the adsorptive capacity of the activated carbon which have been derived from different synthetic waste polymers: The comparison between the composition, structure and the adsorptive behaviour of activated carbons derived from three different types of waste polymers i.e. tire rubber (TR), polyvinyl chloride (PVC), and polyethyleneterephthalate (PET), activated by potassium hydroxide (KOH) ([Carvalho et al., 2003](#)). This study also demonstrated that the properties of activated carbons are highly dependent on their precursor polymers. The characterization of the 3 activated carbons exhibited that the activated carbon with PET as the precursor exhibited the largest surface area which is the result of the uniform aromatic structure followed by the activated carbon with PVC as the precursor. The complex composition and high ash content of tire particles resulted in activated carbon product with significantly lower surface area and heterogeneous pore effective radii. The sorption potential of the activated carbon (PET as the precursor) is the highest due to the high oxygen content and high mesoporous structures. The

method of preparation was carbonization at temperatures above 600 degree Celsius under nitrogen steam stream followed by the activation by KOH.

The work also discusses that the raw material was a sample of industrial waste which had been previously treated with sulphuric acid (10%) at room temperature, washed up to pH 7, dried at 80 C and finally sieved to obtain the fraction of cork particles smaller than 0.0297mm (Carvalho et al., 2003). The work discusses the experiments which involved the mixing of the cork powder with KOH in different ratios (from 0.1:1 to 4:1). The observation which had been made is that the initial increase in the ration was beneficial for the surface area of the AC but as soon as the ration crossed 1 the opposite effect was observed, since the value of the apparent surface area decreased progressively. Recording of the effect of the temperature and time of the calcinations on the surface area of the AC have also been made. Beyond the 1:1 ration the activation progress led to considerable carbon consumption resulting in the decrease in the micropores. The final remark of the work was that the potential of producing good quality activated carbon from waste materials with KOH as activating agent (chemical activation) is noteworthy.

## 2.1 Chromium:

Chromium is one of the most abundant elements in crust of the earth and its valance state ranges from -2 to +6, but it is generally found as trivalent [Cr (III)] and hexavalent chromium [Cr (VI)] in natural environments. Trivalent chromium is the more natural form of chromium which is found in many vegetables, fruits, meat, grains and is often added to multi-vitamins tablets as a dietary supplement, whereas hexavalent chromium (VI) commonly produced by industrial processes and mining of chromium ore, is an environmental contamination indicator. It occurs as salts of chromium, few of which are soluble in water. Chromium (VI) generally exists in monomeric ( $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ ) or dimeric state ( $\text{Cr}_2\text{O}_7^{2-}$ ). The yellow and orange colours of water are due to the presence of monomeric and dimeric species of

chromium discussed above, respectively ([Palmer and Puls, 2004](#)). The general public may have exposure to Cr (VI) ions contaminated drinking waters. Soluble trivalent chromium substances cause eyes and skin irritation, but these effects are related to the acidic nature. If the Cr (VI) aqueous is ingested beyond the tolerable limits then it can be the cause of vomiting, oral ulcers, abdominal pain, indigestion, and severe diarrhoea. Structural damage to DNA can be caused both by soluble and insoluble Cr (VI) compounds, leading to genotoxicity. Studies indicate that Cr (VI) induced DNA damage may result in clastogenesis, altered gene expression, and the inhibition of DNA replication and transcription.

One of the technologies that can overcome these disadvantages is the adsorptive removal of chromium (VI) by various adsorbents. In recent years, numerous scientists have focused on the adsorbents preparation from a variety of waste materials for the contaminants removal from the ecology as the technology not only solves the problem of waste disposal but also converts a potential danger to an invaluable product. Activated carbons adsorption for the contaminants removal has various advantages. Higher quality of effluents i.e. devoid of contaminants can be obtained after treatment ([Mohan et al, 2006](#)).

# **CHAPTER 3**

## **MATERIALS AND METHODS**

### 3.0 MATERIALS AND METHODS:

The raw material (Uncle Chips, a potato chips product package) was obtained from a trash bin within the campus and was process without any cleaning. This would create a situation closer to the real time situation. The chemical composition of the potato chips package is:

- PET: Polyethylene terephthalate.
- PE: Polyethylene.
- MET: Metalized polyester.
- BOPP: Biaxial oriented polypropylene.

#### 3.1 Characterization of activated carbon:

The following characteristic properties of the activated carbon prepared are as follows:

##### 3.1.1 Proximate analysis:

ASTM defines proximate analysis as the determination by prescribed methods of moisture, volatile matter, ash & fixed carbon. The proximate analysis of the given activated carbon sample will be followed by the procedure given below.

- Moisture Content:

A small amount of the sample was put in a petridish or crucible, covered with a lid and weighed using a weighing balance. The crucible was placed in the hot air oven at 105°C with its lid removed & dried for 1.30 hrs. The crucible was taken out, immediately covered with the lid, cooled in a dessicator& weighed.

$$M=100(B-F)/ (B-G) \quad (3.1)$$

Wt of empty petridish =4 2.185 gm = G

Wt of empty petridish + Activated carbon sample (before heating) = B = 52.185 gm

Wt of empty petridish + moisture free sample (after heating) = F = 51.263 gm

% of moisture content (M) = 9.22

- Ash content:

The crucible was ignited in the muffle furnace at 750°C for 1.5 hours. The crucible was placed in the dessicator, cooled to room temperature & weighed. A known amount of the sample which was dried in the hot air oven at 150°C for 3 hours was put in the crucible & the crucible was placed back in the muffle furnace at 750°C for 1.5 hours. The crucible was taken out of the furnace, placed in the dessicator, cooled to room temperature & weighed.

$$A=100(F-G) / (B-G) \quad (3.2)$$

Wt of empty silica crucible = G = 21.433 gm

Wt of empty crucible + activated carbon sample (before heating) = B = 22.433 gm

Wt of empty crucible + ash (after heating) = F = 21.448 gm.

% of ash content=1.5

- Volatile matter content:

A known amount of sample was put in the crucible. The crucible was placed in a muffle furnace at 920°C, covered with lid, & placed for exactly 7 minutes. The crucible was taken out, allowed to cool & weighed.

$$VM=100(100(B-F)-M(B-G))/((B-G)(100-M)) \quad (3.3)$$

Wt of empty crucible with lid= $G=14.003$  gm

Wt of empty crucible + lid + sample(before heating)= $B=15.003$  gm

Wt of empty crucible + lid + sample (after heating)= $F=14.844$  gm

$M$ =Moisture content in %

% of volatile matter content= $7.358$

- Fixed carbon:

% of fixed carbon= $100-(M+A+VM) = 81.922$

### 3.1.2 Field Emission Scanning Electron Microscopy (FESEM):

Field emission Scanning Electron Microscopy (FESEM) is an analytical technique used in materials science to investigate molecular surface structures. Microscopy techniques are used to produce real space magnified images of a surface showing what it looks like. In general microscopy information concerns surface crystallography (i.e. how the atoms are arranged at the surface), surface morphology (i.e. the shape and size of topographic features making the surface), and surface composition (the elements and compounds the surface is composed of).

In FESEM, the phenomenon of field electron emission was used to obtain an image on the detector on the basis of the difference in work function of the various crystallographic planes on the surface.

FESEM produces clearer, less electrostatically distorted images with spatial resolution down to  $1.5\text{nm}$ . that's 3 to 6 times better than conventional SEM. Another advantage of FESEM over SEM is the higher quality and lower voltage image obtained having negligible electrical charging of samples.

### 3.1.3 Iodine Number:

Iodine number is the milligrams of iodine adsorbed by 1 gm of activated carbon from a 0.1N iodine solution when the equilibrium iodine concentration is exactly 0.02N. Iodine number is a measure micro-pore content of the activated carbon. A higher iodine number indicates higher micro- porosity of the sample. ASTM D4607-94(2006) gives the standard procedure for the determination of the iodine number of the activated carbon. 0.7-2 g of dried activated carbon was mixed with 10 ml of 5% by weight & swirled in a conical flask until the activated carbon was wetted. The flask was boiled for 30 sec by placing it on a hot plate. The content of the flask was cooled to room temperature & 100 ml of 0.1 N iodine solution was added on it. The flask was shaken vigorously for 30 sec. The contents were filtered through a filter paper. Initial 20-30 ml of the filtrate was discarded & the remaining filter was collected in a clean beaker. 50 ml of this filtrate was titrated against 0.1 N sodium thio-sulphate solution until yellow colour just disappeared. 1 ml of starch solution was added & titration was carried out till blue colour was just disappeared.

The iodine no was found out to be 719 mg/g.

### 3.1.4 Methylene Blue Number:

Methylene blue number is defined as the milligrams of methylene blue dye adsorbed by 1g of dried activated carbon. It is a measure of the mesopore content of the activated carbon. 1200 mg/l methylene blue stock solution was prepared. The sample was diluted to give solutions of 5 different concentrations ([Hameed et al, 2007](#)). A standard calibration curve was prepared by measuring the absorbance at 664 nm. A known concentration solution was prepared from the stock solution and a known amount of activated carbon was put into it. The flask was placed in a shaker at 25°C for 24 hours at 115 rpm. The absorbance of the resulting solution was measured at 664 nm and the concentration was calculated from the calibration plot.

### 3.1.5 Fourier Transform Infrared (FTIR) Spectroscopy:

The activated carbon's chemical structure can be investigated by the FTIR spectroscopy technique. Infrared spectroscopy (IR) is a technique in a variety of forms which provides information about surface functional groups ([Friedel and Hofer, 1970](#); [Friedel and Carlson, 1972](#); [Ishazaki and Marti, 1981](#)).

The computerized Fourier-transform infrared spectroscopy (FTIR) has several advantages over the generic dispersive spectroscopy. An interferometer is used by the FTIR in replacement of a grating or slits. This results in the higher energy availability, of the order of 100 to 200 times over the dispersive system. More precise information is provided by this technique which also allows the lower concentrations measurement of surface functional groups. The main advantages of FTIR over the conventional techniques are the availability of higher energy throughout; the multiplex capability, and the frequency scale's higher accuracy ([Chiang et al., 2002](#); [Jaramillo et al., 2010](#)).

### 3.2 Hydrothermal Carbonization:

It is a well-known fact that the thermal combustion of organic polymers results in the formation of charred residues and air Bourne particulate smoke along with toxic emissions of PAHs, PCDDs and PCDFs. The later groups are formed from the multitude of functionalities comprising “softeners” such as phthalates, antioxidants like phenols, organophosphatides, UV-stabilizers such as amines and piperidyl esters and antistatic agents such as ethoxylated amines, heat stabilizers such as organotins and pigments ([Poerschmann et al, 2014](#)).

The formation of the Polycyclicdibenzodioxins (PCDDs) and PCDFs under certain circumstances in aqueous solutions containing chlorinated organic compounds is been seen in

many experiments with polymers like PVC and they have to be tested for in the present work which are usually formed between 180 °C and 260°C.

In the present times, the main sources of the waste food packaging polymeric solids are the landfills/dumping grounds. The main method of the reduction of their volumes is incineration which produces toxic gases as well as release inorganic chlorine causing corrosion in the furnace. Thus, a reliable alternative method to treat waste polymers safely and efficiently in an environmentally sound manner is worth pursuing. HTC is expected to meet these requirements.

The method used for the carbonization is Hydrothermal Carbonization (HTC) which had been discovered in less than a decade and was used only for the carbonization of biomass under high pressure and temperature. The HTC is an alternative method of carbonization which prevents the formation of ash due to the high temperature of generic carbonization. The high pressure and its corresponding temperature provide the necessary condition for the carbonization process to take place.

1 gram of the raw material was taken and the package was cut similar to filings. The temperature chosen was 235°C and the duration of the charring was chosen to be 15 hours. The volume of the container was 200mL and it was filled up to 70% of its volume for the process along with the raw material. After 5 hours of charring thrice, the hydrochar was taken out of the muffle furnace and was collected in a vessel. Subsequently, it was left to cool down and dry for 10 hours ([Poerschmann et al, 2014](#)).

The dried hydrochar after cooling was measured to be 0.3 grams.

### 3.3 Treatment with Soxhlet Apparatus:

A soxhlet apparatus is a piece of laboratory apparatus which was invented originally for the extraction of lipids from a solid material. Typically, the limited solubility of a certain solid in

the solution attracts the utilization of the Soxhlet extraction apparatus, and the impurity is insoluble or sparingly soluble in that chosen solvent. Generally, a solid material which contains the desired compound is placed inside a thick filter paper material called thimble, which is placed in the main chamber of the Soxhlet apparatus. The extraction solvent to be used is taken into a distillation flask and the soxhlet extractor is now placed onto the flask. The soxhlet is then equipped with a water condenser.

For the refluxing, the solvent is fed with heat. The vapours of the solvent move up the distillation arm and flood into the chamber in which the thimble is kept filled with solid. The condenser makes sure that all the solvent vapour cools, and drips back down into the chamber in which the solid material is kept. The chamber which contains the solid material is gradually filled up with the heated solvent. Some of the undesired compound will then dissolve in the heated solvent. When the soxhlet chamber is almost full, the chamber empties itself with the help of a siphon side arm, with the solvent running back down to the distillation flask.

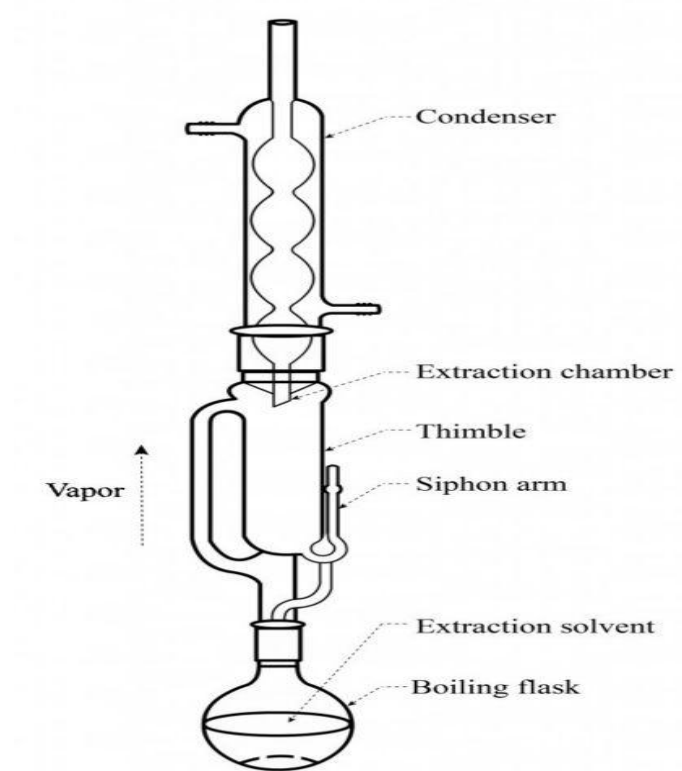


Figure 3: Soxhlet Apparatus.

The thimble ensures that the fast movement of the heated solvent but it doesn't transport any solid material to the still pot. This cycle is allowed to be repeated many times, over hours or even days. During each cycle, a part of the undesired non-volatile compound dissolves in the solvent in the flask. After numerous cycles the desired compound is concentrated in the thimble. The advantage is that instead of many portions of the warm solvent being passed through the sample; just one batch of solvent is refluxed.

The hydrochar was then treated with Benzene in the Soxhlet apparatus for the removal of rust, ash particles and chlorides. The temperature was chosen to be 80°C and the duration was chosen to be 4 hours. This process was repeated twice. It was observed that the ash content was other impurities were collected in benzene. The hydrochar was again weighted and was found out to be 0.12 grams in weight suggesting the fact that the impurities like iron rust and ash content were in present in the hydrochar.

### 3.4 Activation of the hydrochar with 1 M Potassium Hydroxide (KOH) solution:

Activation was done by completely submerging the processed hydrochar into the 1 M KOH solution so a period of 10 hours and then the activated carbon was taken out for the drying process which took 5 days to complete and the temperature was set as 70°C.

### 3.5 Chemicals used:

Chemicals used were conc. HCl (for washing the pressure vessel), Benzene solution, 1 M KOH solution, Resublimed Iodine, Methylene Blue (solid), Chromium (solid) and distilled water. The methods used for the preparation are Hydrothermal Carbonization (HTC), and Refluxing (Soxhlet apparatus).

### 3.6 Instrumentation:

An automated shaker was used for all the adsorption experiments. A UV-ray spectrophotometer was used to determine the absorbance. Glass wares & conical flask were used to handle the solutions. A meter balance was used to weigh the samples. Pipette was taken in transferring the solution into the test tube to record the adsorbance of solution.

#### 3.6.1 Fabrication of the pressure vessel:

The hydrothermal carbonization required a pressure vessel which will develop temperature driven pressure. A section of pipe of 1.5 inches nominal diameter was chosen and the material of construction was iron.

One of the ends of the hollow pipe was welded with a metal sheet of the same diameter and a thickness of 10mm. The other end of the pipe was welded to a piece of connecting pipe whose other end was of diameter 1 inch. The 1 inch end of the connecting pipe was first fixed into one of the ends of a high pressure gate valve; whose material of construction was zinc incorporated iron, and then welded so as to avoid any scope of leakage.

Gas welding was utilized at all the joints for complete air proofing. In order to reinforce maximum air proofing, the welding joints and the site of the gate, vacuum gel was applied whose temperature was  $-100^{\circ}\text{C}$  to  $250^{\circ}\text{C}$ .

The constructed pressure vessel is shown below:



Figure 4: Fabricated Equipment.

### 3.7 Experimental Work:

#### 3.7.1 Hydrothermal Carbonization:

For the hydrothermal carbonization, the pressure vessel was kept in the muffle furnace for at  $250^{\circ}\text{C}$  so that all the chloride and chlorine content is removed by itself but at that temperature, leakage from the gate was observed and also at that temperature, the vacuum gel couldn't work as its operating temperature had been exceeded.

Thus, again, the temperature was set to be  $235^{\circ}\text{C}$ . At this temperature, after five hours of duration in the muffle furnace, the water level was checked in the vessel and was found that

the water level had reduced by 30%. Thus, to maintain the water levels additional water was added after every 5 hours. The total time duration was 15 hours.

### 3.7.2 Methylene Blue number:

Total 5 samples of methylene blue were made from the stock solution. The concentrations of methylene blue in the solutions were 100ppm, 150ppm, 200ppm, 250ppm and 175ppm. The UV-spectrophotometer was used to calculate the adsorbance, at wavelength 664nm for the first four solutions (100ppm, 150ppm, 200ppm, 250ppm). The solution with 175ppm was used for calculating the methylene blue number.

In the first experiment, 200 mg of activated carbon was added to the 175ppm methylene blue solution and then was kept in the shaker for 24 hours at 125rpm. It was observed that all the methylene blue was adsorbed and a clear solution was obtained which did not give any useful information.

In the second experiment keeping the other parameters unchanged, the amount of activated carbon used was only 100 mg. It was observed that almost all the methylene blue had been adsorbed from the solution. It infers that the activated carbon prepared has high mesopore content and has high adsorption capacity.

# **CHAPTER 4**

## **RESULT AND DISCUSSION**

## 4.0 RESULTS AND DISCUSSION:

### 4.1 Fourier Transform Infrared Spectroscopy (FTIR) analysis:

In the current work, FTIR analysis was used to determine the bonds which were present in the activated carbon prepared. Bonds which were found out were expected as they were either in their precursor i.e. the food packaging polymer or were introduced in the activation process. Though the presence of chlorine in the activated carbon was unwanted and its presence shows that the temperature for the carbonization should be above 235°C for the complete removal of the chlorine from the activated carbon sample prepared. The FTIR analysis graph is given below:

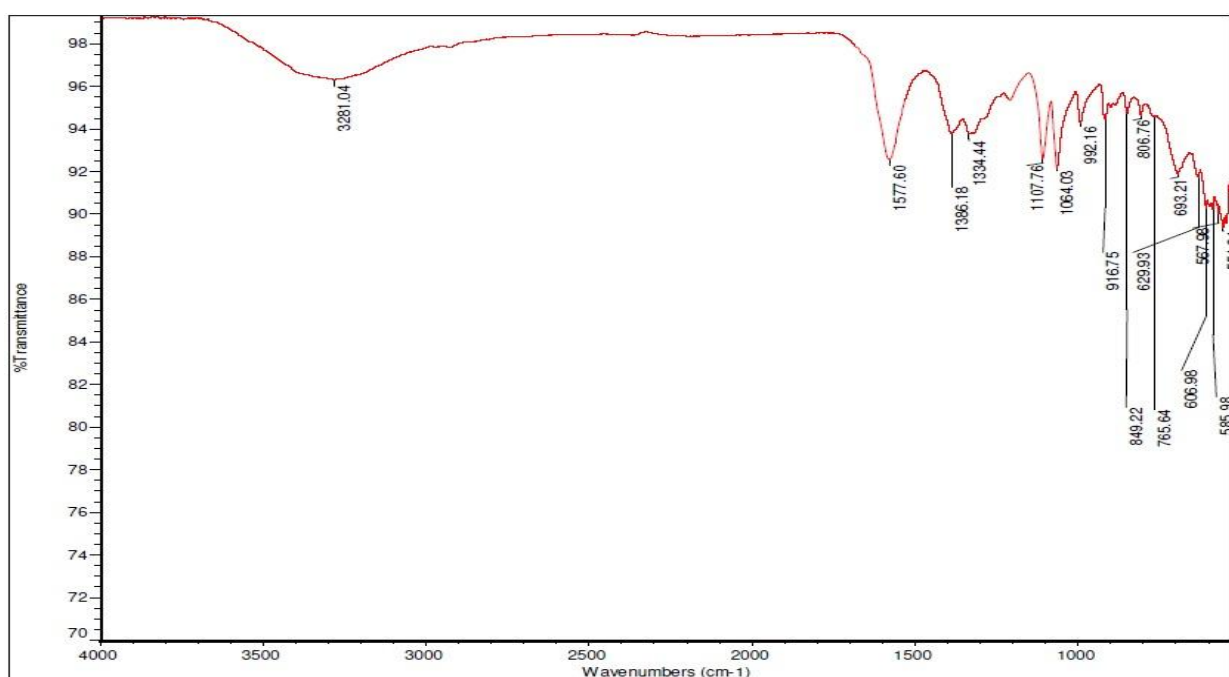


Figure 5: FTIR analysis graph

The following table gives the corresponding bonds of the peaks obtained in the FTIR spectroscopy analysis:

Table 2: FTIR analysis corresponding bonds

Peak	Bond
3281.04	$-OH$
1577.60	$-C=C-$
1386.18	$-C-H$
1107.76	$-C-O-$
1064.03	$-C-O-$
992.16	$=C-H-$
916.75	$=C-H-$
849.22	$=C-H-$
806.76	$=C-H-$
765.64	$-C-Cl-$
693.31	$=C-H-$
629.93	$-C-Cl-$

The reasons for presence of the bonds shown in the table are as follows:

- The  $-OH$  and  $-C-O-$  bonds are expected due to the activation with KOH and the stabilizing chemicals which are present in the parent raw material.
- $-C=C-$ ,  $=C-H-$ ,  $-C-H-$  bonds are present due to the polymeric nature of the raw materials. These bonds could be found in both aromatic and aliphatic structures.
- $-C-Cl-$ , again is found in the raw materials as perhaps one of the major stabilizer agent.

## 4.2 Iodine Number:

The commercial grade activated carbon which is manufactured has an average iodine number which is greater than 1000. It is known that higher the iodine number, higher is the adsorption capacity. The general range of iodine number of a good quality activated carbon is from 500 to 1200. The iodine number of the activated carbon prepared for the current work is 719 which indicate good adsorption capacity given the fact that the activated carbon has been prepared from unprocessed waste food packaging polymers. Also, it shows the decent micropore network formation. It has been observed that the iodine number could be a parameter which could approximately determine the surface area per unit gram of the activated carbon prepared. So, it could be approximated with minor scope of error that the surface area of the activated carbon prepared would be close to  $719\text{m}^2/\text{g}$  as for the iodine number ranging from 200-850mg/g the surface area is approximately same as the iodine number.

## 4.3 Methylene Blue number:

As it was discussed before, methylene blue number determines the mesopore content in the activated carbon prepared. Higher the methylene blue number higher would be the mesopore content in the activated carbon prepared. The amount used for the procedure was 100mg. The following table gives the absorbance of the solutions with various concentrations of methylene blue.

Table 3: Methylene Blue conc. v/s absorbance

Concentration	Absorbance
50	8.80
100	18.34
150	25.48
200	29.33
250	46.02
175	0.363

The linear fitting curve for the graph plotted is found out to be:

$$y = 0.1709 \cdot x - 0.035 \quad (4.1)$$

The methylene blue number for the activated carbon prepared is 17.3 g per 100gms of activated carbon. The methylene blue number of a good quality activated carbon is within the range of 11-28. It is apparent that the activated carbon prepared is of good quality and contains high mesopore content. The graph which was obtained from the tabulated data is given:

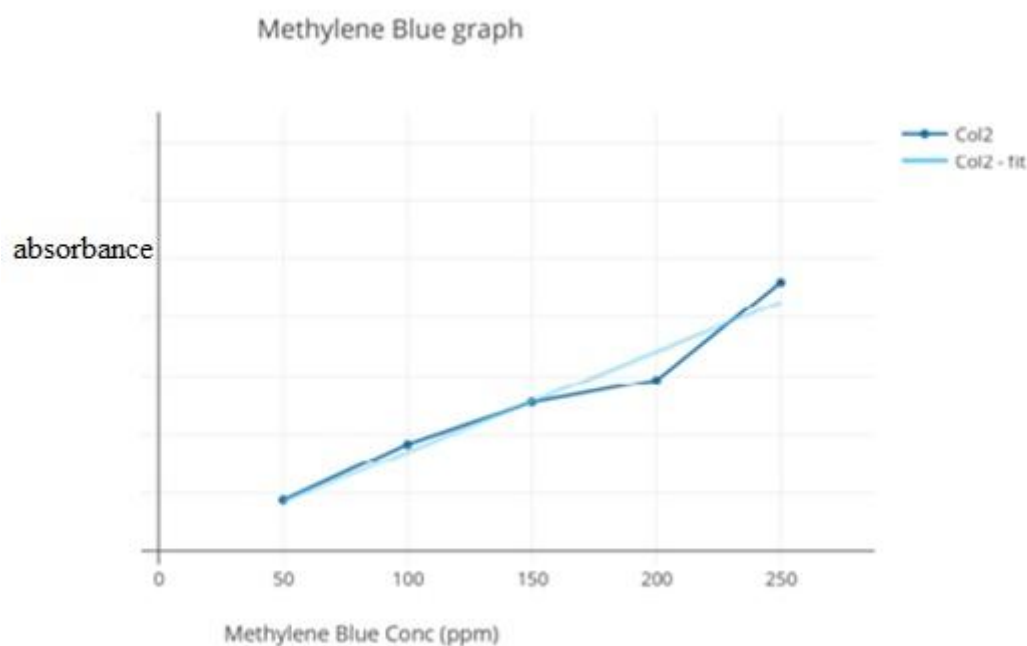


Figure 6: Methylene Blue concentration v/s absorbance graph

#### 4.4 Field Emission Scanning Electron Microscope (FESEM) analyses:

The FESEM images are used to determine if there is any non-uniformity in the particle shapes, sizes, and particle structures. Also, it is utilized to observe the pores which have been formed. Though multiple images give a clearer picture of the effect of various parameters on the activated carbon prepared, here the scope of the work was only to prepare the activated carbon and characterize it. FESEM was chosen over SEM as the images are sharper and clearer. From the images it is observed that the size distribution of the particles is diasporic i.e. the particles of the activated carbon are present in wide range of sizes and shapes. Other aspect which is observed is that the surface of the activated carbon particles is quite rough and is in stacked form and the other just like a “loose sponge”. The FESEM analysis gave the following images.

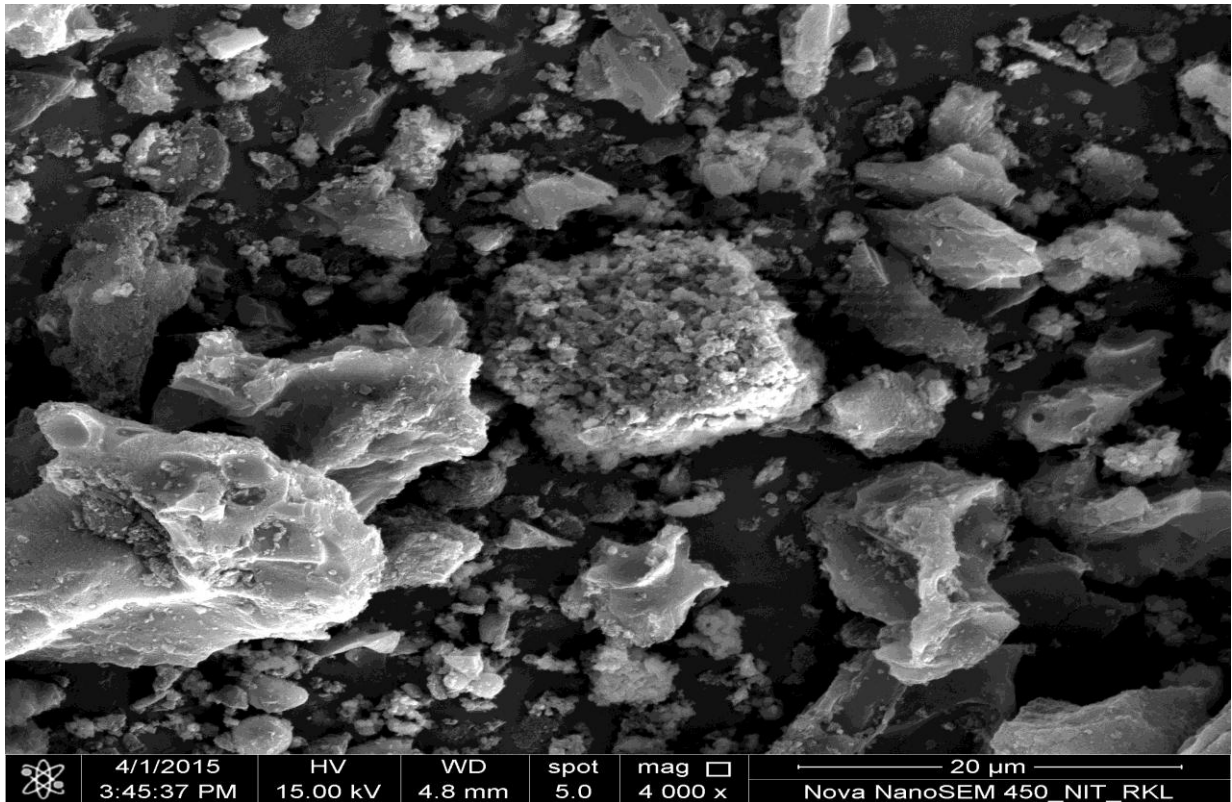


Figure 7: FEM image (20 micrometers)

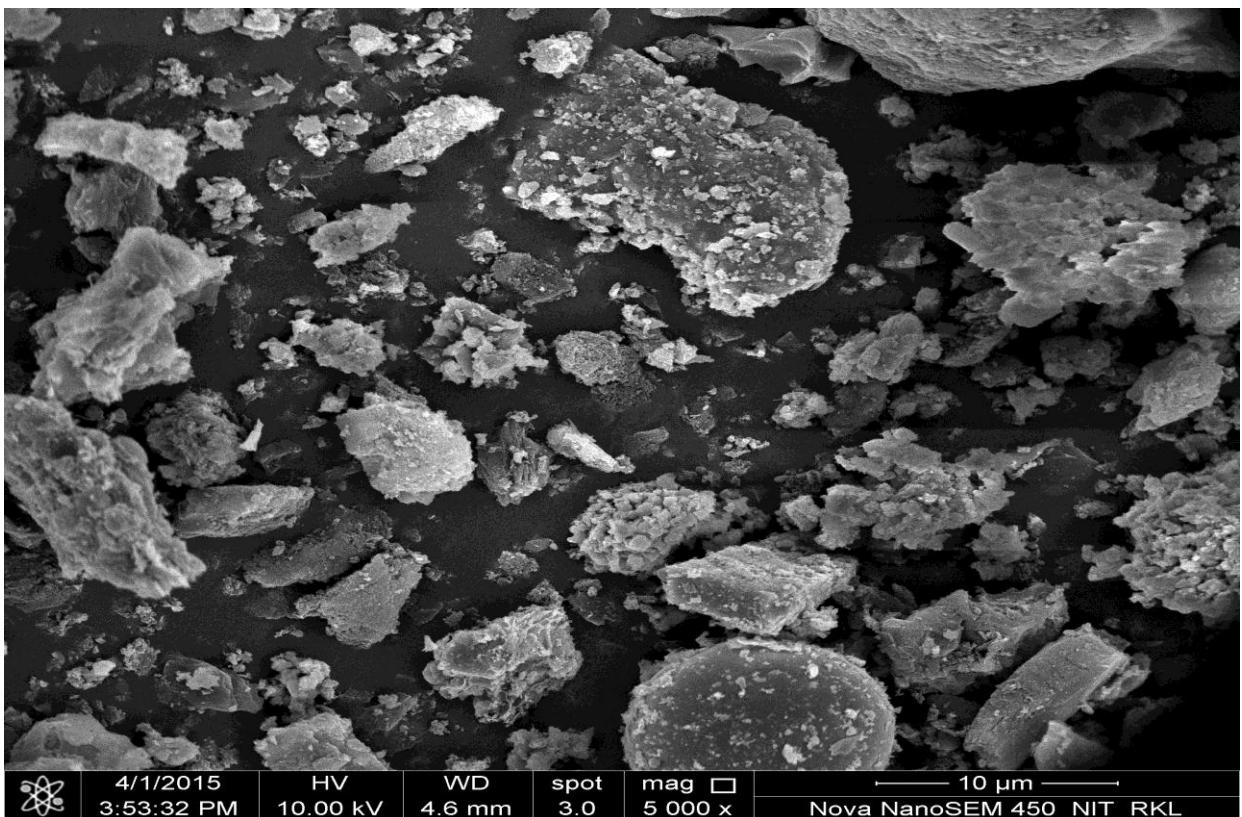


Figure 8: FEM image (10 micrometers)

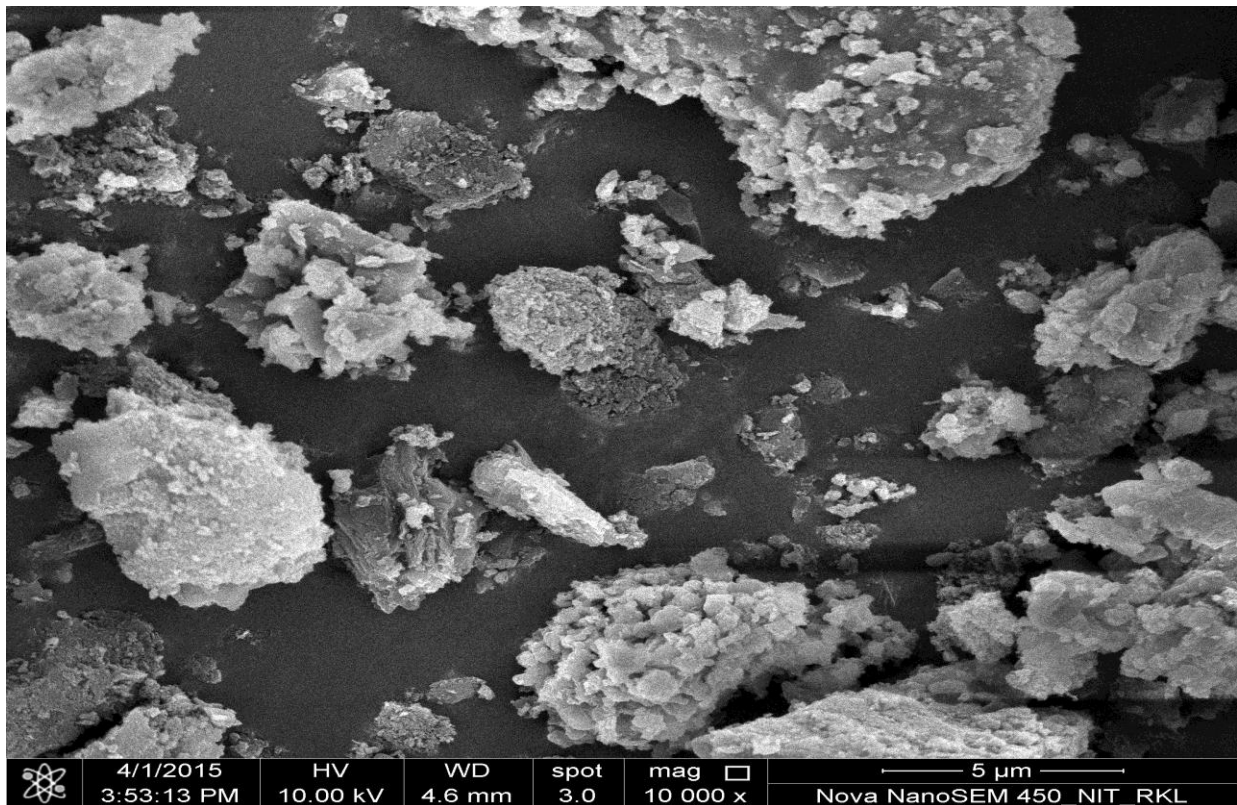


Figure 3: FEM image (5 micrometers)

#### 4.5 Proximate analysis of Activated Carbon:

The proximate analysis of the activated carbon prepared determined that the percentage of the fixed carbon is 95.42% which is an appreciable amount thus suggesting that the activated carbon present is of appreciable quality which is also seconded by the fact that the percentages of ash, moisture and volatile content is low.

Table 4: Tabulated Proximate analysis results

<b>Content</b>	<b>Percentage</b>
Ash	1.38
Moisture	1.73
Volatile	1.47
Fixed Carbon	95.42

# **CHAPTER 5**

## **CONCLUSION**

## 5.0 CONCLUSION:

The many characterization techniques like Proximate Analysis, Field Emission Scanning Electron Microscopy (FESEM), Iodine number, and Methylene Blue Number were carried out. Through FESEM, the structure of the surface of the activated carbon prepared was observed to be rough and stacked in nature and also observed was the wide range in the particle size distribution. The surfaces appeared to have large number of pores of various shapes.

With the help of the proximate analysis it was observed that the activated carbon has close to 96% carbon which seconds the claim that the activated carbon prepared is of appreciable quality.

The iodine number also suggested that the activated carbon has good adsorption capacity as the iodine number was found out to be 719.

The activated carbon has high adsorptive capacity which is concluded from the fact that 200mg of activated adsorbs all the methylene blue from the solution of 175ppm solution in a duration of 24 hours and 172ppm when 100mg is used for adsorption keeping the duration same.

The FTIR analysis results were in complete agreement the predictions made of the bonds which were suspected in the activated carbon which were either present due to their presence in the precursor or due to their introduction in the activation of the hydrochar. The analysis also suggested that the complete removal of chlorine had not been possible and requires some additional step for its removal and higher temperature of hydrothermal carbonization.

To circumscribe, the activated carbon prepared from waste food packaging polymers presents itself as a potential solution for two major problems namely voluminous plastic accumulation and high levels of chromium (VI) in the industrial waste waters.

## 5.1 Future work:

The further work should be carried out:

- On complete removal of chlorine from the hydrochar.
- On the analysis of the water used for the HTC process.
- On the analysis of the benzene, used as the solvent for the extraction process using the help of soxhlet extractor.
- The effect of parameters on adsorption of chromium (VI) can also be studied to determine the optimum consitions.

# **CHAPTER 6**

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## 6.0 REFERENCES:

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