

A

PROJECT REPORT ON

**Production and characterization of Activated
Carbon produced from a suitable Industrial
sludge**

A REPORT SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
BACHELOR OF TECHNOLOGY (CHEMICAL ENGINEERING)

Submitted By

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CERTIFICATE

This is to certify that that the work in this thesis report entitled “**Production and characterization of activated carbon produced from a suitable industrial sludge**” submitted by **Subhashree Pradhan** in partial fulfillment of the requirements for the degree of Bachelor of Technology in Chemical Engineering, Session 2007-2011 in the department of Chemical Engineering, National Institute of Technology, Rourkela, is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge the matter embodied in the report has not been submitted to any other University /Institute for the award of any degree.

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Abstract:

The purpose of this study is the preparation of activated carbon using a suitable industrial sludge. The characterization of two types of industrial sludges showed that paper sludge was a better option over rice husk. The activated carbon produced from pyrolysis of paper mill sludge was chemically activated with various activating agents like zinc chloride, potassium hydroxide and potassium chloride. A systematic investigation of the effect of impregnation ratio, activation temperature and activation time on the properties of the activated carbon was done. The chemically activated carbons were characterized by measuring iodine and yield percentage. The activated carbon prepared from paper mill sludge in this study had maximum iodine of 764.80 mg/g with $ZnCl_2$ as the activating agent. The FT-IR analysis depicts the presence of a variety of functional groups. The XRD analysis reveals that the produced activated carbon has low content of inorganic constituents compared with the precursor.

Keywords: Activated carbon, Paper sludge, Impregnation ratio FT-IR analysis, XRD analysis

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CHAPTER 1

INTRODUCTION

1.Introduction

Activated carbon, also widely known as activated charcoal or activated coal is a form of carbon which has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions.^[1] The word active is sometimes used in place of activated. Due to such high degree of micro porosity , just 1 gram of activated carbon has a surface area in excess of 500 m² (about one tenth the size of an American football field), as typically determined by nitrogen gas adsorption. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment generally enhances the adsorbing properties of the material. Activated carbon is most commonly derived from charcoal.

1.1 Preparation of activated carbon:

Activated carbon is nothing but carbon produced from carbonaceous source materials like nutshells, peat, wood, coir, lignite, coal and petroleum pitch. It can be produced by any one of the following described processes:

a) Physical reactivation: by this process precursor is developed into activated carbons using gases. This is generally done by using one or a combination of the following processes:

Carbonization: Material having appreciable carbon content is pyrolyzed at temperature ranging between 600–900 °C, in the absence of oxygen (usually in inert atmosphere with gases like argon or nitrogen)

Activation/Oxidation: in this process raw material or carbonized material is exposed to oxidizing atmospheres (carbon monoxide, oxygen, or steam) at temperatures above 250 °C, usually in the temperature range of 600–1200 °C.

b) Chemical activation: Before carbonization, the raw material can be impregnated with certain chemicals. The chemical needs to be typically an acid, strong base, or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, zinc chloride, respectively). After impregnation, the raw material needs to be carbonized at lower temperatures (450–900 °C). It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material

1.2 Objective of the project :

Different surface analyses is to be used in this study to evaluate the effect of production processes on the physical characteristics of the produced carbons.

The significant feature of sludge-based activated carbon that makes it a unique and a particularly economical adsorbent is that it can be produced from waste materials such as paper mill sludge or even the rice husk disposed of as waste from rice mills. A current problem faced by pulp mills is the generation of an excessive amount of sludge during the paper making process and secondary treatment of wastewater. For environmental and ecological reasons, the innocuous disposal of these sludges has become immensely important. Optimization of the processes involved with the conversion of paper mill sludge or rice husk to activated carbon provides an innovative, environmentally safe, and economically feasible solution to the problem of sludge management at paper mill facilities. Sludge to carbon conversion processes can significantly reduce the sludge volume produced in the paper mill industry or the rice mills, eliminate the need for further treatment of sludge, reduce the cost of hauling and land filling the sludge, and reduce transportation costs.

The emphasis of this study is to optimize processes involved with the production of activated carbons with prescribed surface properties (micro- or meso porous structure) and specific end uses from paper mill sludge. The higher purity (when compared to bio-solids), negative cost, high rate of production, and strong carbonaceous structure of paper mill sludge and rice husk makes them both useful as a precursor for carbon production.

CHAPTER 2

LITERATURE REVIEW

2. Literature review

Activated carbons are carbonaceous materials that can be distinguished from elemental carbon by the oxidation of the carbon atoms found on the outer and inner surfaces.^[5] These materials are characterized by their extraordinary large specific surface areas, well-developed porosity and tunable surface-containing functional groups^[6]. For these reasons, activated carbons are widely used as adsorbents for the removal of organic chemicals and metal ions of environmental or economic concern from air, gases, potable water and wastewater.^[7] The surface oxygen functional groups can be easily introduced to the carbon by different activation methods including dry and wet oxidizing agents. Dry oxidation methods involve the reaction with hot oxidizing gas such as steam and CO₂ at temperatures above 700 C.^[8] Wet oxidation methods involve the reaction between the carbon surface and solutions of oxidizing agents such as phosphoric acid H₃PO₄, nitric acid HNO₃, hydrogen peroxide H₂O₂, zinc chloride ZnCl₂, potassium permanganate KMnO₄, ammonium persulphate (NH₄)₂SO₈, potassium hydroxide KOH, etc. From the above oxidizing agents, phosphoric acid and zinc chloride are usually used for the activation of lignocellulosic materials, which have not been carbonized before.^[9] On the other hand, potassium hydroxide is usually used to activate coal or chars precursors. It has been reported that zinc chloride produces activated carbon with higher specific area than that produced by using phosphoric acid.^[10] However, phosphoric acid activation is widely preferred over zinc chloride because ZnCl₂ has bad environmental impact and the activated carbon produced when using it can not be used in the food and pharmaceutical industries.^[11] Activated carbon usually increases the cost of the treatment process. Its economical drawback has stimulated the interest to utilize cheaper raw materials for the production of activated carbon.^[12]

Consequently, a wide variety of agricultural by-products and wastes has been investigated as cellulosic precursors for the production of activated carbon in addition to hard wood and bituminous coal. These precursors include coconut shell and wood^[13], Olive stones^{[14],[15]}, sugarcane bagasse,^[16] pecan shells^[17], palm seed,^[18] apple pulp,^[19] rubber seeds^[20] and molasses.^[21] Commercial activated carbons are commonly produced from naturally occurring carbonaceous materials such as coal, wood and peat.^[22] Due to the growing need for activated carbons in our society and the high cost of raw materials and production, many researchers have attempted various wastes such as tires,^[23] resins,^[24] agricultural byproducts^{[25]; [26],[27]} and dried sewage sludge^{[28],[29]} as raw materials and proposed new production methods^{[30],[31]} for activated carbons with potential applications in pollution control. Furthermore, more interest has been devoted to utilize some wastes of carbonaceous materials such as paper mill sludge^[32], old newspapers^[33] and waste tires^[34]. Recently, activated sludge has been produced as a result of wastewater treatment activities and has emerged as an interesting option for the production of activated carbon.^{[35],[36]} The results reported in these studies indicate that chemical activation of the sewage sludge with $ZnCl_2$ and H_2SO_4 produced activated carbon of high adsorption capacity comparable with that of commercial activated carbon. In addition, the choice of a cheap precursor for the production of activated carbon means both considerable savings in the production cost and a way of making use of a waste material, thus reducing its disposal problem.^[37]

The sewage sludge used in the previous investigations is characterized by its carbonaceous nature and its high content of volatile compound. However, this sludge seems to contain appreciable quantities of inorganic impurities as it comes from urban treatment plants. Therefore,

sulphuric acid seems to be suitable as a chemical activation agent because it is able to dissolve the majority of inorganic impurities found in the sludge.

Activated carbons are increasingly used as an economic and stable mass separation agent for the removal of surfactants to raise the final product quality in many industrial processes. Activated carbons also play an important role in many areas of modern science and technology such as purification of liquids and gases, separation of mixtures, and catalysis.^[38] Adsorption of activated carbon is governed by the chemical nature of the aqueous phase, the solid phase, and the chemical nature of the adsorbing organic.^[39]

According to Torregrosa-Macia et al.^[40], for a given industrial application, a solid adsorbent with a relatively wide pore size distribution can be obtained solely through a chemical activation process. Physical activation can further enhance the adsorbent's pore structure due to a partial oxidation of the carbonized material by gases such as CO/CO₂ or steam.^{[41],[42]}

Analysis of the surface physical properties of the carbon includes determination of the total surface area, extent of microporosity, and characterization of the pore size distribution. Nitrogen adsorption isotherms are commonly used for these types of surface analyses.^{[43], [44], [45] and [46]} The measured relative pressure and adsorbed volume of nitrogen gas are commonly used in various mathematical models (i.e. BET model) to calculate the monolayer coverage of nitrogen adsorbed on the adsorbent surface, while the characteristics of the pore structure and pore distribution can be identified from comparative plots such as 't' and 'α_s'-plots.^{[47],[48],[49] and [50]} The extent of the microporosity is commonly evaluated by applying low-pressure isotherm data to the Dubinin–Radushkevich (DR) equation.^{[47],[51]} The pore size distribution and the corresponding surface

areas of the mesoporous adsorbents are traditionally calculated from the hysteresis loop according to the BJH theory, which is based on the Kelvin equation. ^{[49], [50]}

2.1 Classification:

Activated carbons are complex products which are difficult to classify on the basis of their behaviour, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics.

Powdered activated carbon (PAC)

A micrograph of activated charcoal under bright field illumination on a light microscope. Notice the fractal-like shape of the particles hinting at their enormous surface area. Each particle in this image, despite being only around 0.1 mm wide, has a surface area of several square metres. This image of activated charcoal in water is at a scale of 6.236 pixels/ μm , the entire image covers a region of approximately 1.1 by 0.7mm. Traditionally, active carbons are made in particulate form as powders or fine granules less than 1.0 mm in size with an average diameter between .15 and .25 mm.^[21] Thus they present a large surface to volume ratio with a small diffusion distance. PAC is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieve. Granular activated carbon is defined as the activated carbon being retained on a 50-mesh sieve (0.297 mm) and PAC material as finer material, while ASTM classifies particle sizes corresponding to an 80-mesh sieve (0.177 mm) and smaller as PAC. PAC is not commonly used in a dedicated vessel, owing to the high head loss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters.

Granular activated carbon (GAC)

Granular activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapors as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodorization and separation of components of flow system. GAC can be either in the granular form or extruded. GAC is designated by sizes such as 8×20, 20×40, or 8×30 for liquid phase applications and 4×6, 4×8 or 4×10 for vapor phase applications. A 20×40 carbon is made of particles that will pass through a U.S. Standard Mesh Size No. 20 sieve (0.84 mm) (generally specified as 85% passing) but be retained on a U.S. Standard Mesh Size No. 40 sieve (0.42 mm) (generally specified as 95% retained). AWWA (1992) B604 uses the 50-mesh sieve (0.297 mm) as the minimum GAC size. The most popular aqueous phase carbons are the 12×40 and 8×30 sizes because they have a good balance of size, surface area, and head loss characteristics.

Extruded activated carbon (EAC)

Extruded activated carbon combines powdered activated carbon with a binder, which are fused together and extruded into a cylindrical shaped activated carbon block with diameters from 0.8 to 130 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

Impregnated carbon:

Porous carbons containing several types of inorganic impregnant such as iodine, silver, cations such as Al, Mn, Zn, Fe, Li, Ca have also been prepared for specific application in air pollution

control especially in museums and galleries. Due to antimicrobial/antiseptic properties, silver loaded activated carbon is used as an adsorbent for purification of domestic water. Drinking water can be obtained from natural water by treating the natural water with a mixture of activated carbon and $\text{Al}(\text{OH})_3$, a flocculating agent. Impregnated carbons are also used for the adsorption of H_2S and thiols. Adsorption rates for H_2S as high as 50% by weight have been reported.

Polymer coated carbon:

This is a process by which a porous carbon can be coated with a biocompatible polymer to give a smooth and permeable coat without blocking the pores. The resulting carbon is useful for hemoperfusion. Hemoperfusion is a treatment technique in which large volumes of the patient's blood are passed over an adsorbent substance in order to remove toxic substances from the blood.

Other: Activated carbon is also available in special forms such as cloths and fibres. The "carbon cloth" for instance is used in personnel protection for the military.

2.2 Properties of activated carbon:

A gram of activated carbon can have a surface area in excess of 500 m^2 , with 1500 m^2 being readily achievable.^[3] Carbon aerogels, while more expensive, have even higher surface areas, and are used in special applications.

Under an electron microscope, the high surface-area structures of activated carbon are revealed. Individual particles are intensely convoluted and display various kinds of porosity; there may be many areas where flat surfaces of graphite-like material run parallel to each other, separated by only a few nanometers or so. These micropores provide superb conditions for adsorption to

occur, since adsorbing material can interact with many surfaces simultaneously. Tests of adsorption behaviour are usually done with nitrogen gas at 77 K under high vacuum, but in everyday terms activated carbon is perfectly capable of producing the equivalent, by adsorption from its environment, liquid water from steam at 100 °C and a pressure of 1/10,000 of an atmosphere.

James Dewar, the scientist after whom the Dewar (vacuum flask) is named, spent much time studying activated carbon and published a paper regarding its absorption capacity with regard to gases.^[4] In this paper, he discovered that cooling the carbon to liquid nitrogen temperatures allowed it to absorb significant quantities of numerous air gases, among others, that could then be recaptured by simply allowing the carbon to warm again and that coconut based carbon was superior for the effect. He uses oxygen as an example, wherein the activated carbon would typically absorb the atmospheric concentration (21%) under standard conditions, but release over 80% oxygen if the carbon was first cooled to low temperatures.

Physically, activated carbon binds materials by van der Waals force or London dispersion force.

Activated carbon does not bind well to certain chemicals, including alcohols, glycols, strong acids and bases, metals and most inorganics, such as lithium, sodium, iron, lead, arsenic, fluorine, and boric acid.

Activated carbon does adsorb iodine very well and in fact the iodine number, mg/g, (ASTM D28 Standard Method test) is used as an indication of total surface area.

2.3 Applications of activated carbon:

Activated carbon is used in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air and many other applications.

Recently Activated Carbon filters have gained popularity among recreational users of Cannabis, and other smoking herbs for their use in effectively filtering out "Tar" from the smoke. They are becoming quick competition for Vapourizers as they are only a fraction of the cost and achieve nearly the same thing.

One major industrial application involves use of activated carbon in the metal finishing field. It is very widely employed for purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions. A variety of organic chemicals are added to plating solutions for improving their deposit qualities and for enhancing properties like brightness, smoothness, ductility, etc. Due to passage of direct current and electrolytic reactions of anodic oxidation and cathodic reduction, organic additives generate unwanted break down products in solution. Their excessive build up can adversely affect the plating quality and physical properties of deposited metal. Activated carbon treatment removes such impurities and restores plating performance to the desired level.

Activated carbon, in 50% w/w combination with celite, is used as stationary phase in low-pressure chromatographic separation of carbohydrates (mono-, di- trisaccharides) using ethanol solutions (5–50%) as mobile phase in analytical or preparative protocols.

In environment field activated carbon adsorption has numerous applications in removing pollutants from air or water streams both in the field and in industrial processes such as spill cleanup, Groundwater remediation , Drinking water filtration , Air purification , Volatile organic compounds capture from painting, dry cleaning, gasoline dispensing operations, and other processes.

In medical applications activated carbon is used to treat poisonings and overdoses following oral ingestion. It is thought to bind to poison and prevent its absorption by the gastrointestinal tract. In cases of suspected poisoning, medical personnel administer activated charcoal on the scene or at a hospital's emergency department. Dosing is usually empirical at 1 gram/kg of body mass (for adolescents or adults, give 50–100 g), usually given only once, but depending on the drug taken, it may be given more than once.^[4] In rare situations activated charcoal is used in Intensive Care to filter out harmful drugs from the blood stream of poisoned patients. Activated charcoal has become the treatment of choice for many poisonings, and other decontamination methods such as ipecac-induced emesis or stomach pumping are now used rarely.

CHAPTER 3

PRECURSOR SELECTION

3. PRECURSOR SELECTION:

Precursor (raw material) selection for the production of activated carbon was obviously the first step of the project. Conventionally, activated carbon is produced from carbonaceous source material such as wood, peat, coal, and wastes of vegetable origin (e.g. nutshells, fruit stones). Today, one promising approach for the production of cheap and efficient activated carbon is the reuse of waste sludge, such as bio solids produced at municipal or industrial wastewater treatment facilities. The usage of waste sludge is especially important due to its mass production and resulting occupation of valuable landfill space.

The two types of industrial sludge available as choices for precursor were:

- Rice husk (Bargarh paper mill)
- Paper sludge (JK paper mill, Rayagada)

To decide the superiority of a precursor over the other characterization of the precursor was done using various methods like:

- CHNS elemental analyser
- Proximate analysis

3.1 CHNS elemental analyser:

CHNS elemental analysers provide a means for the rapid determination of carbon, hydrogen, nitrogen and sulphur in organic matrices and other types of materials. They are capable of

handling a wide variety of sample types, including solids, liquids, volatile and viscous samples, in the fields of pharmaceuticals, polymers, chemicals, environment, food and energy.

The analysers are often constructed in modular form such that they can be set up in a number of different configurations to determine, for example, CHN, CHNS, CNS or N depending on the application. This adaptability allows not only flexibility of operation but also the use of a wide range of sample weights from a fraction of a milligram to several grams (macro-systems.)

In its simplest form, simultaneous CHNS analysis requires high temperature combustion in an oxygen-rich environment and is based on the classical Pregl-Dumas method. This combustion can be carried out under both static conditions i.e. introduction of a set volume of oxygen or dynamic conditions i.e. a constant flow of oxygen for a set period of time. Often, catalysts are also added to the combustion tube in order to aid conversion.

Basic principles

In the combustion process (furnace at ca. 1000^oC), carbon is converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/ oxides of nitrogen and sulphur to sulphur dioxide. If other elements such as chlorine are present, they will also be converted to combustion products, such as hydrogen chloride. A variety of absorbents are used to remove these additional combustion products as well as some of the principal elements, sulphur for example, if no determination of these additional elements is required.

The combustion products are swept out of the combustion chamber by inert carrier gas such as helium and passed over heated (about 600^o C) high purity copper. This copper can be situated at the base of the combustion chamber or in a separate furnace. The function of this copper is to remove any oxygen not consumed in the initial combustion and to convert any oxides of nitrogen

to nitrogen gas. The gases are then passed through the absorbent traps in order to leave only carbon dioxide, water, nitrogen and sulphur dioxide.

Detection of the gases can be carried out in a variety of ways including (i) a GC separation followed by quantification using thermal conductivity detection (ii) a partial separation by GC ('frontal chromatography') followed by thermal conductivity detection (CHN but not S) (iii) a series of separate infra-red and thermal conductivity cells for detection of individual compounds. Quantification of the elements requires calibration for each element by using high purity 'micro-analytical standard' compounds such as acetanilide and benzoic acid.

Applications of CHNS Elemental Analysers

CHNS elemental analysers have been used in analytical laboratories for over thirty years. The method is used extensively across a wide range of applications, including pharmaceuticals, chemicals, oil-related products, catalysts and food. In the oil industry, an important application is the regular monitoring of coke build-up on refinery catalysts to ensure that regeneration procedures (involving controlled burning of the carbon) are executed at optimal intervals. Since many of these catalyst systems involve large quantities of noble metals such as platinum, palladium and rhenium, mismanagement of this testing would entail serious financial losses. In food analysis, the determination of nitrogen (as a surrogate for protein) is very important for pricing grain and evaluating meat products, and is increasingly undertaken by combustion analysis.

3.2 Proximate Analysis:

The proximate analysis of a substance is a simple means of determining the distribution of products obtained when the coal sample is heated under specified conditions. As defined by ASTM D 121, proximate analysis separates the products into four groups: (1) moisture, (2) volatile matter, consisting of gases and vapors driven off during pyrolysis, (3) fixed carbon, the nonvolatile fraction of coal, and (4) ash, the inorganic residue remaining after combustion. Proximate analysis is the most often used analysis for characterizing a material in connection with their utilization.

Volatile matter:

The sample was measured and placed in a closed crucible. It was then heated upto 925 C for exactly 7.5 min in a furnace. The crucible was then cooled in a desiccator and weighed

Ash content:

Sample was measured and taken in a crucible. It was then heated to 750 C for 1.5 hr. During this test the crucible was left open. After the required heating, the crucible was cooled in a desiccator and then weighed.

Moisture content:

Sample was measured and taken in a petri dish. It was spread nicely on the dish. It was then heated at 105 C for 1.5 hr. the petri-dish was left open during the heating process. After heating petri-dish was removed, cooled in desiccator and then weighed.

CHAPTER 4

PREPARATION AND

CHARACTERIZATION OF

ACTIVATED CARBON

4. Preparation and characterization of activated carbon:

4.1 preparation of activated carbon :

A pure, mesoporous activated carbon was produced following the procedure developed by Walhof and Khalili et al.^[52]. The prescribed process of production of activated carbon is as below:

- Raw sludge was first dried in an oven at 110°C for 24 h, then crushed manually. Crushing provided smaller particles with increased surface area and also enabled more efficient chemical activation of the raw material.
- Samples were sieved after crushing to obtain particle sizes smaller than 600 µm.
- Chemical activation of the sludge was then done using different activating agents like ZnCl₂, KOH and KCl. To ensure a complete reaction between activating agent and sludge particles, slurries of the sludge and activating agent were mixed at 85°C for 7 hrs with a magnetic stirrer.
- After chemical activation, samples were dried at 110°C for about 10–36 h (depending on the required impregnation time).
- After drying, the sludge was crushed again into a fine powder. And activated samples were exposed to light and humidity (L&H) for about 22 h to enhance the development of the pore structure during pyrolysis. The aforementioned steps promote uniform carbonization reactions during the pyrolysis
- The dried, chemically activated, and light and humidity treated sludge was placed into a quartz reactor. The pyrolysis was carried out under a flow of nitrogen gas (70 ml/min) at 500-800 °C (depending on the set activation temperature) for 1 to 2 h (depending on the

decided activation time). The temperature was reached at a rate of approximately 20 °C per min. Nitrogen gas was used to provide an inert atmosphere and to carry volatile matter away from the heating zone. Upon completion of the pyrolysis, sample was removed from the reactor and crushed using mortar and pestle.

- Upon completion of the pyrolysis, the sample was removed from the reactor and crushed.
- Pyrolysis was followed by rinsing using 500 ml of 1.2 M HCl, and 500 ml of distilled water to remove excess activating agent and residual inorganic matter.
- Then the chemical activated product was dried and stored for characterization.

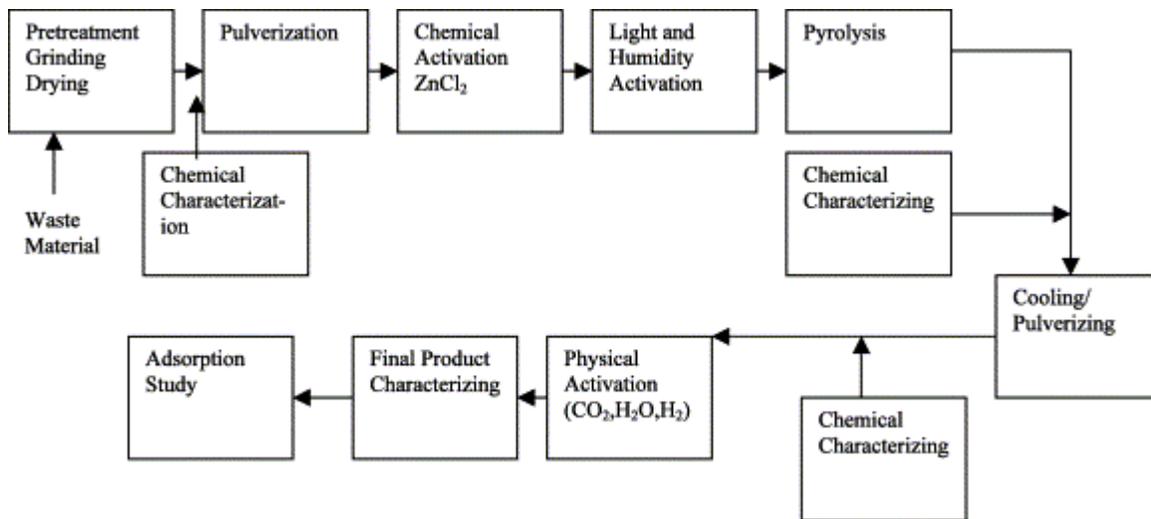


Fig. 1. Steps involved with the production of activated carbon from paper mill sludge.

4.2 characterization of activated carbon produced:

4.2.1 iodine value of the activated carbon:

To gain further knowledge of the porous structure of activated carbon, iodine adsorption from liquid phase was adopted by other researchers^[53] in the characterization of sludge-based activated carbons. The adsorption of aqueous I₂ is considered a simple and quick test for evaluating the surface area of activated carbons associated with pores larger than 1 nm.^[54] The iodine value, defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration of 0.02 N, was measured according to the procedure established by the American Society for Testing and Materials (ASTM 2006). The mean values of data for each experiment were presented. Standard deviation was calculated from triplicate samples.

Iodine Number is accepted as the most fundamental parameter used to characterize activated carbon performance. It gives the measure of activity level (higher number indicates higher degree of activation). It indicates the micropore (0 – 20 Å) content

Reagents used in the iodine value test are as listed below:

- ❖ 0.1N Iodine solution (40 gm KI in 1 Ltr of Distilled water).
- ❖ 0.05N Sodium Thiosulphate solution (12.5 gm Na₂S₂O₃·5H₂O in 1 Ltr Distilled water)
- ❖ 1% Starch solution
- ❖ Activated carbon

Procedure of the iodine value test:

I Standardisation of Iodine solution

* 10c.c of 0.1N Iodine solution was taken in conical flask.

* 2 drops of Starch solution was added to it.

- * The pale yellow colour of Iodine Soln turned Blue.
- * Titration of the formed solution was done with 0.05 N Sodium Thiosulphate till it becomes Colourless.
- * Burette reading corresponds to blank reading.(B)

II

- * 0.2 gm of Activated carbon was weighed very accurately.
- * It was introduced into the Iodine flask which should be completely dry .
- * 40cc of 0.1N Iodine solution was then added.
- * The flask was shaken properly for 4 minutes and then filtered.
- * The filtrate was collected in a dry flask and then 10cc of the filtrate was titrated against Standard Sodium thiosulphate solution using starch as indicator
- Burette reading corresponds to (A)

Calculations involved in iodine value estimation:

Iodine value: $C \times \text{Conversion factor}$; mg/gm

Factor: $\text{Mol wt. of iodine (127)} \times \text{normality of iodine} \times 40 / \text{Wt. of carbon} \times \text{Blank reading}$

$C=B-A$

4.2.2 Other physical properties of activated carbon:

The apparent density of the material was obtained by weighting five grams of the produced activated carbon and transferring it into a 10 mL graduated cylinder. The cylinder was tamping with a rubber pad while activated carbon was being added until the entire original sample was

transferred to the cylinder. Tamping was continued for 5 minutes until there was no further settling produced. The volume was recorded and the apparent density was calculated on the dry basis:

Ash content was measured by burning the produced activated carbon in a muffle furnace at 973 K. One gram of dry carbon was transferred into a crucible and then placed in the furnace for four hours. The difference between the original and final weight of the carbon represents the ash content per gram.

Moisture content was also obtained by weighing 10 grams of the carbon and placed in an oven at 105 C for 3 h. Then the carbon was cooled in the absence of humidity and reweighed again. The difference between the initial and final mass of the carbon represents the water content in the sample.

The yield of activated carbon product was calculated based on the chemical-impregnated sludge dried at 105 C.

The composition of C, H and N in the activated carbon used as raw material was determined using an elemental analyzer (PE-2400 II, Perkin-Elmer Corp., USA).

4.2.3 X-Ray Diffraction Measurements:

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and

wavelength or energy. X-ray diffraction yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system. The most comprehensive description of scattering from crystals is given by the dynamical theory of diffraction. Single-crystal X-ray diffraction is a technique used to solve the complete structure of crystalline materials, ranging from simple inorganic solids to complex macromolecules, such as proteins. Powder diffraction (XRD) is a technique used to characterise the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. It may also be used to characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds and, when coupled with lattice refinement techniques, such as Rietveld refinement, can provide structural information on unknown materials. Powder diffraction is also a common method for determining strains in crystalline materials. An effect of the finite crystallite sizes is seen as a broadening of the peaks in an X-ray diffraction as is explained by the Scherrer Equation. Thin film diffraction and grazing incidence X-ray diffraction may be used to characterize the crystallographic structure and preferred orientation of substrate-anchored thin films. High-resolution X-ray diffraction is used to characterize thickness, crystallographic structure, and strain in thin epitaxial films. It employs parallel-beam optics. X-ray pole figure analysis enables one to analyze and determine the distribution of crystalline orientations within a crystalline thin-film sample. X-ray rocking curve analysis is used to quantify grain size and mosaic spread in crystalline materials.

X-ray diffraction spectroscopy (XRD) analyses were carried out with PANalytical X-ray, Philips

Analytical. A dried sample of the produced material is grinded using an agate mortar and pestle and tested at 40kV and 40mA. The spectra were analyzed using PC-APD diffraction software.

4.2.4 Fourier Transform Infrared Spectroscopy:

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments. FTIR is commonly used to identify chemicals from spills, paints, polymers, coatings, drugs and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. We have several infrared spectral libraries including on-line computer libraries. To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and/or other techniques.

FTIR analysis was made using IPRrestige-21, FTIR-84005, SHIMADZU Corporation (Kyoto, Japan). Sample of 0.1 g was mixed with 1 g of KBr, spectroscopy grade (Merk, Darmstadt, Germany), in a mortar. Part of this mix was introduced in a cell connected to a piston of a hydraulic pump giving a compression pressure of 15 kPa / cm². The mix was converted to a solid disc which was placed in an oven at 105 C for 4 hours to prevent any interference with any existing water vapor or carbon dioxide molecules. Then it was transferred to the FTIR analyzer and a corresponding chromatogram was obtained showing the wave lengths of the different functional groups in the sample which were identified by comparing these values with those in the library.

4.2.5 Scanning electron microscope analysis:

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathode luminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-

dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown to the right. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample. In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB_6) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters or the thermally-assisted Schottky type, using emitters of zirconium oxide. The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in

diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronised with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor and saved to a computer's hard disk.

Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. Unlike optical and transmission electron microscopes, image magnification in the SEM is not a function of the power of the objective lens. SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen. Provided the electron gun can generate a beam with sufficiently small diameter, a

SEM could in principle work entirely without condenser or objective lenses, although it might not be very versatile or achieve very high resolution. In a SEM, as in scanning probe microscopy, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, or the voltage supplied to the x, y deflector plates, and not by objective lens power.

CHAPTER 5

RESULTS AND

DISCUSSIONS

5. Result and discussion:

5.1 Result of elemental analysis and proximate analysis of the sludges:

From the CHNS analysis and proximate analysis it was clearly seen that there was not much difference in the fixed carbon content. Hence both are viable options for activated carbon production. But the mass per unit volume of paper sludge being much higher than that of rice husk, it would be more economical to choose paper sludge as the precursor of activated carbon production. Hence paper sludge is fixed as our precursor in the further production and analysis of activated carbon.

Table 1: Result of elemental analysis of rice husk and paper sludge

Element	Rice husk (%)	Paper sludge (%)
Carbon	38.7	39.52
hydrogen	5	4.53
Oxygen	36	19.22
Nitrogen	.7	.5
Sulphur	.1	.11
Chlorine	0	0.2

Table 2. proximate analysis of the precursor

component	Rice husk (wt%)	Paper sludge (wt%)
Volatile matter	64.7	21.3
Fixed carbon	15.7	50.11
Ash content	19.2	14.5
Moisture content	.4	14.09

5.2 Effect of chemical activating agents on activated carbon productuced

In chemical activation, different activating agents are expected to significantly affect the extent of activation .^[55] In the present study, activating with ZnCl₂, KOH and KCl were evaluated and compared. Table 3 shows the effect of different activating agents on the iodine value and yield of activated carbon from sludge in N₂ atmosphere at 600 C for 1 h. The concentration of various chemical activating agents was fixed at 1 N and the impregnation time for these agents was maintained as 20 h. The iodine values of the activated carbons changed significantly with activating agents. The activation with ZnCl₂ gave the highest yield of 18.4%. More over, the ZnCl₂ activated product had the highest iodine value of 664.8mg/gm, indicating that its pore surface and structure were the best developed. Thus, ZnCl₂ was chosen as the activating agent for subsequent experiments.

Table 3: Effect of various activating agent on the yield and iodine number.

Activating agent	Concentration of agent (N)	Iodine value (mg/gm)	Yield(wt%)
ZnCl ₂	1	664.8	18.4
KOH	1	649.7	11.7
KCl	1	556.3	15.3

5.3 Effect of concentration of ZnCl₂ solution used for producing activated carbons

The yields and iodine values of activated carbons prepared from paper sludge in N₂ atmosphere at 600C for 1 h are presented in figure 2 . The impregnation process was carried on with various concentrations of ZnCl₂ solution but identical solid sludge by dry weight of 6.2 g for a fixed impregnation time of 20 h prior to activation. The iodine values of activated carbons produced had an optimum value of 764.8mg/gm, and the corresponding ZnCl₂ concentration was 2N. When the concentration was decreased to 1 M, the iodine value was relatively low because of insufficient ZnCl₂ to react with the sludge to efficiently create the internal pore structures. However, if the concentration of ZnCl₂ was as high as 3N or more, the micropore structure of activated carbon deteriorated due to excessive carbonization. The yield of product decreased steeply from 18.6 to 11.9% in the concentration range with increasing iodine value, which was probably due to the formation of more micropores in the product. The extent of decrease in product yield was lower at higher concentrations of activating agents. In all, we considered the ZnCl₂ concentration of 2 N to be optimum.

Hence, it was used in subsequent experiments.

Table 4: Effect of concentration of activating agent on iodine value and yield of activated carbon.

Conc of ZnCl ₂	Iodine value (mg/g)	Yield %
1N	692.4	18.6
2N	764.3	12.4
3N	607.7	11.9
4N	546.3	9.22

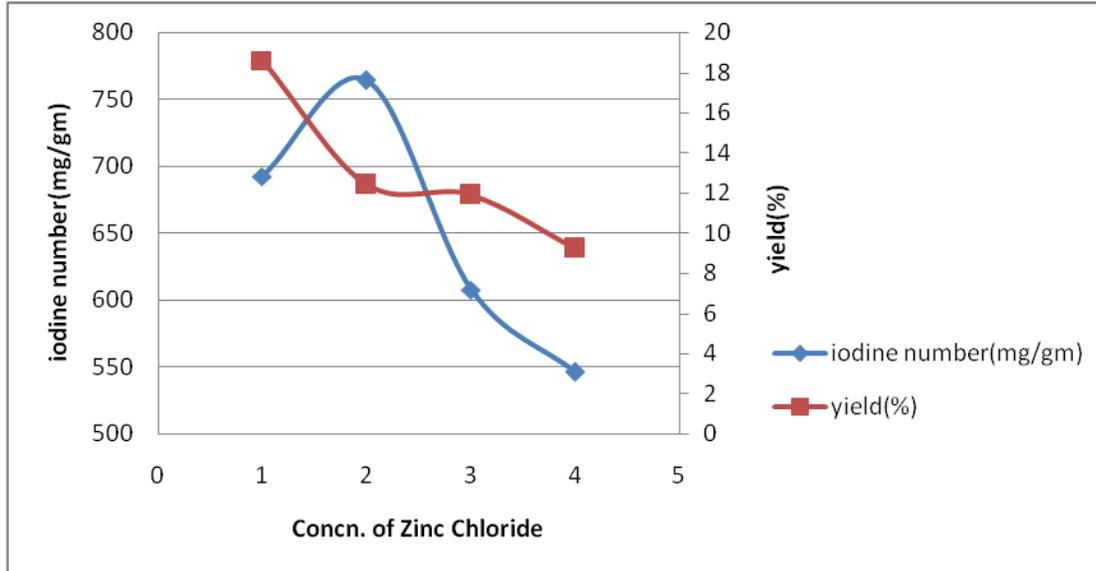


Figure 2: Effect of concentration of activating agent on yield percent and iodine value of activated carbon.

5.4 Effect of time of impregnation on activated carbon products

The effect of impregnation time on the iodine value of the activated carbon product was shown in figure 3 . Paper sludge was used and activated at 600 C for 1 h. The iodine values of samples increased gradually with time of impregnation, and leveled off after 20 h. Long impregnation time would promote the diffusion of $ZnCl_2$ in the sludge. When the time was extended to 20 h, equilibrium was attained in the mixture of paper sludge and $ZnCl_2$. Hence, the impregnation time of 20 h was required and was used in subsequent experiments.

Table 5 : Effect of impregnation time on Iodine value

Impregnation time (h)	Iodine value (mg/gm)
10	602.67
15	754.8
20	764.3
25	767.7
30	768.3

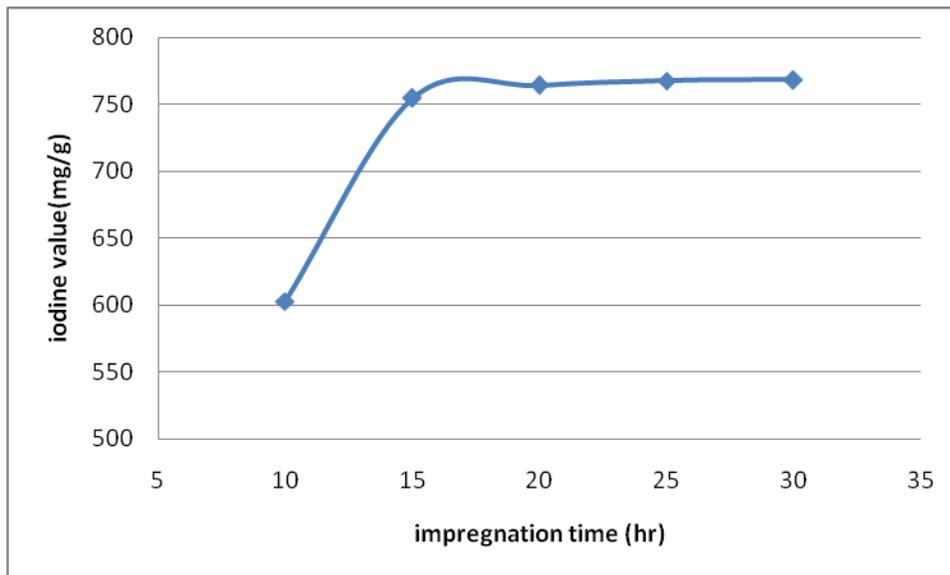


Figure 3: Effect of impregnation time on iodine value of activated carbon

5.5 Effect of activation temperature on activated carbon products

The activation temperature is a very influential parameter on the pore structure of activated carbon, which determines the adsorption capacity.^[56] The variation in iodine values of activated carbon product was investigated as a function of activation temperature. Paper sludge was used as raw material and activation time was fixed at 1 h. As shown in Figure 4, the iodine value increased progressively with activation temperature, and then decreased when the temperature exceeded 600 C. At higher temperature (.600C), the pore walls between adjacent pores were probably destroyed and the micropores were destructed, which led to the decrease in iodine value of the activated carbon. Thus, it can be concluded that the optimum temperature for the production of activated carbons from paper sludge is approximately 600C.

Table 6: Effect of activation temperature on iodine value of activated carbon

Activation temp (c)	Iodine value (mg/g)
500	543.2
550	678.9
600	769.5
700	589.9
800	561.6

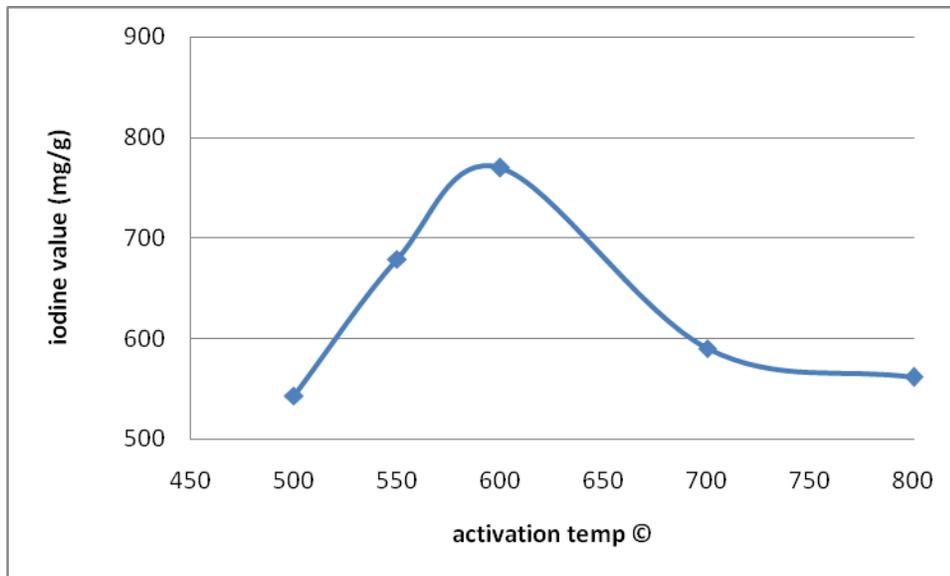


Figure 4: Effect of activation temperature on iodine value of the activated carbon

5.6 Effect of activation time on activated carbon products

The variations in iodine value of the activated carbon produced from paper sludge versus the activation time are shown in Figure 5. The iodine values were measured as 690.9 and 764.8mg/ g after 30 min and 1 h of activation time, respectively. Thereafter, the iodine value gradually dropped to a value of 574.3mg/gm at 3 h. The decrease in iodine value for the time period of 1–3 h is considered to be due to the extended activation of product, resulting in the conversion of some micropores into mesopores and mesopores into macropores. This trend indicates that the activation time of 1 h is optimum in our study.

Table 7: Effect of activation time on iodine value of activated carbon produced.

Activation time (min)	Iodine value (mg/g)
30	690.9
60	764.8
90	704.6
120	616.9
180	574.8

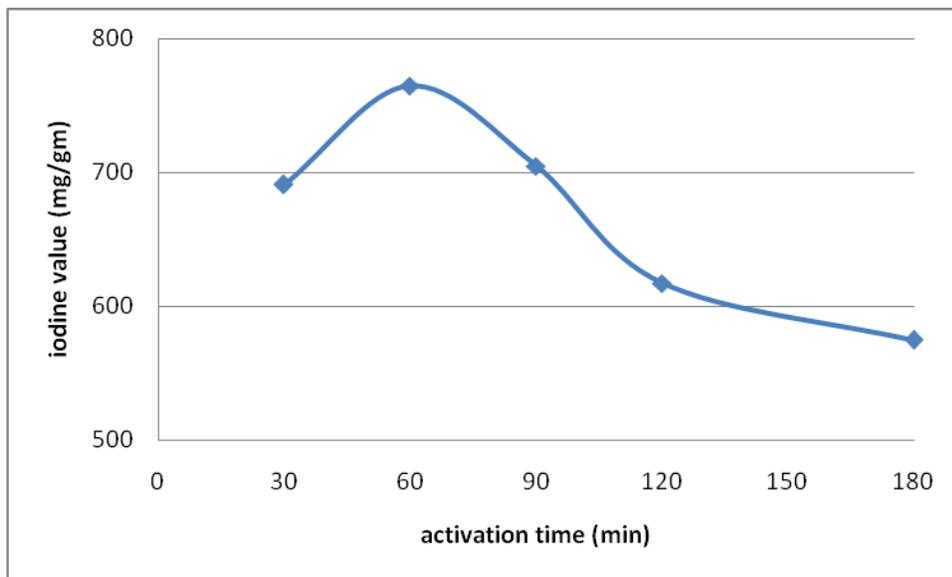


Figure5: Effect of activation time on iodine value of activated carbon

5.7 FT-IR analysis:

The FT-IR spectroscopic study of the produced carbon is shown in Figure 6. The sample showed four major absorption bands at 2900-3500 cm⁻¹, 1300-1750 cm⁻¹, 1000-1250 cm⁻¹ and 450-750 cm⁻¹. A wide band with two maximum peaks can be noticed at 2930 and 3450 cm⁻¹. The band at 3450 cm⁻¹ is due to the absorption of water molecules as result of an O-H stretching mode of hydroxyl groups and adsorbed water, while the band at 2930 is attributed to C-H interaction with the surface of the carbon. However, it must be indicated that the bands in the range of 3200-3650 cm⁻¹ have also been attributed to the hydrogen-bonded OH group of alcohols and phenols.^{[57],[58]}

In the region 1300-1750 cm⁻¹, amides can be distinguished on surface of the activated carbon which has two peaks at 1640 and 1450 cm⁻¹. These functional groups were obtained during the activation process as a result of the presence of ammonia and primary amines that usually exist in the sludge. Moreover, the band at 1500 cm⁻¹ may be attributed to the aromatic carbon-carbon stretching vibration. The two peaks at 1125-1150 cm⁻¹ yield the fingerprint of this carbon. The sharp absorption band at 1125 cm⁻¹ is ascribed to either Si-O^[59] or C-O stretching in alcohol, ether or hydroxyl groups.^{[60],[61]} The band at 1150 cm⁻¹ can also be associated with ether C-O symmetric and asymmetric stretching vibration (-C-O-C- ring)^[62]. This band could also be attributed to the antisymmetrical Si-OSi stretching mode as a result of existing alumina and silica containing minerals within the sludge samples^[63]. The region 450-750 cm⁻¹ show two bands in the 480 and 485 cm⁻¹ which are associated with the inplane and out-of-plane aromatic ring deformation vibrations^[64]. Peaks at 598 and 680 cm⁻¹ are assigned to the out-of-plane C-H bending mode. These spectra were also suggested to be due to alkaline groups of cyclic ketons and their derivatives added during activation^{[60],[65]}.

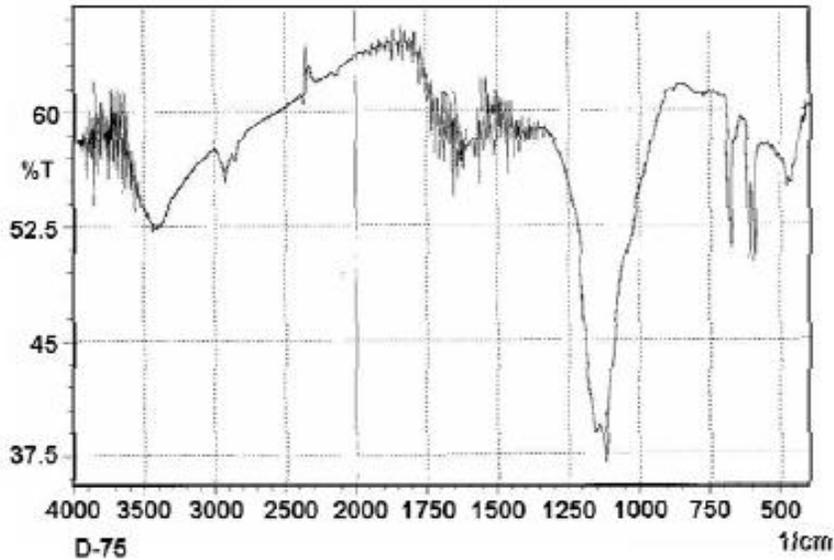


Figure 6: FT-IR spectrum for activated carbon from sludge

5.8 XRD analysis:

X-ray diffractograms for both the activated sludge and activated carbon are shown in Figures 3 and 4. The XRD spectra of the activated sludge illustrated the presence of different aluminosilicate minerals. Zeolite X-Y was observed at $2\theta = 29.4$ with relative intensity of 158 cps, followed by faujasite detection at $2\theta = 26.50$. Other peaks were located at $2\theta = 32.9$, 35.9 and 39.40 for mullite, hematite and quartz, respectively. While the rest of the peaks for

sodalite, analcime and sodium silicates re located at $2\theta = 43.1, 47.5$ and 48.5 ,

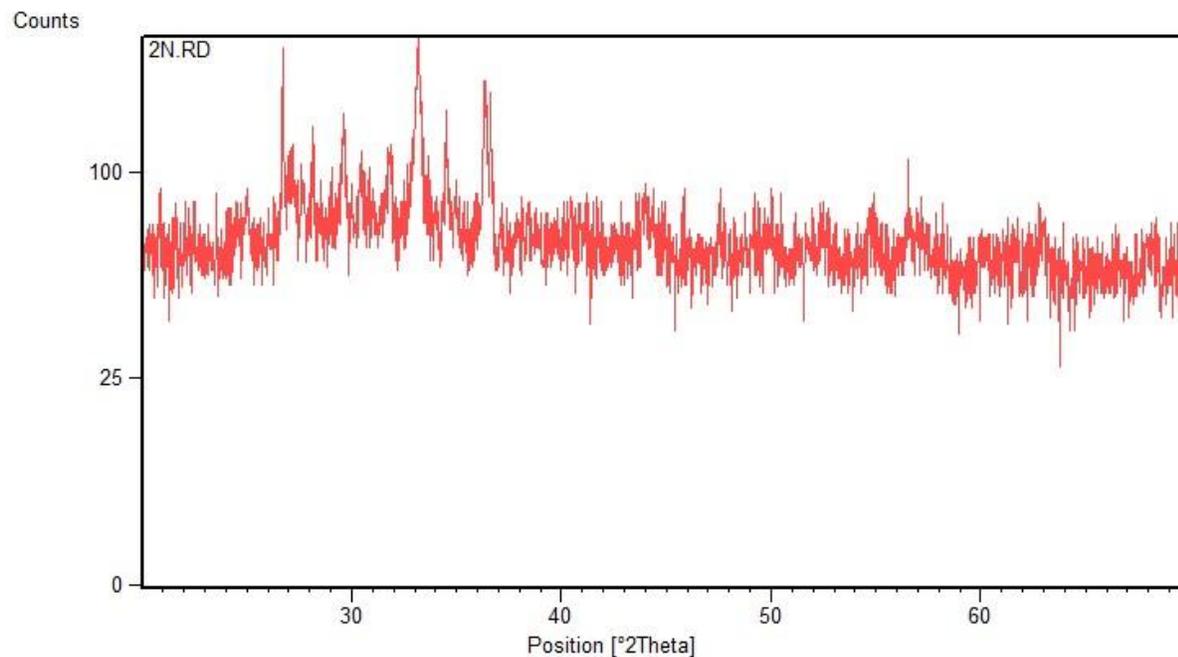


Figure 7: X-ray diffractogram for sludge sample

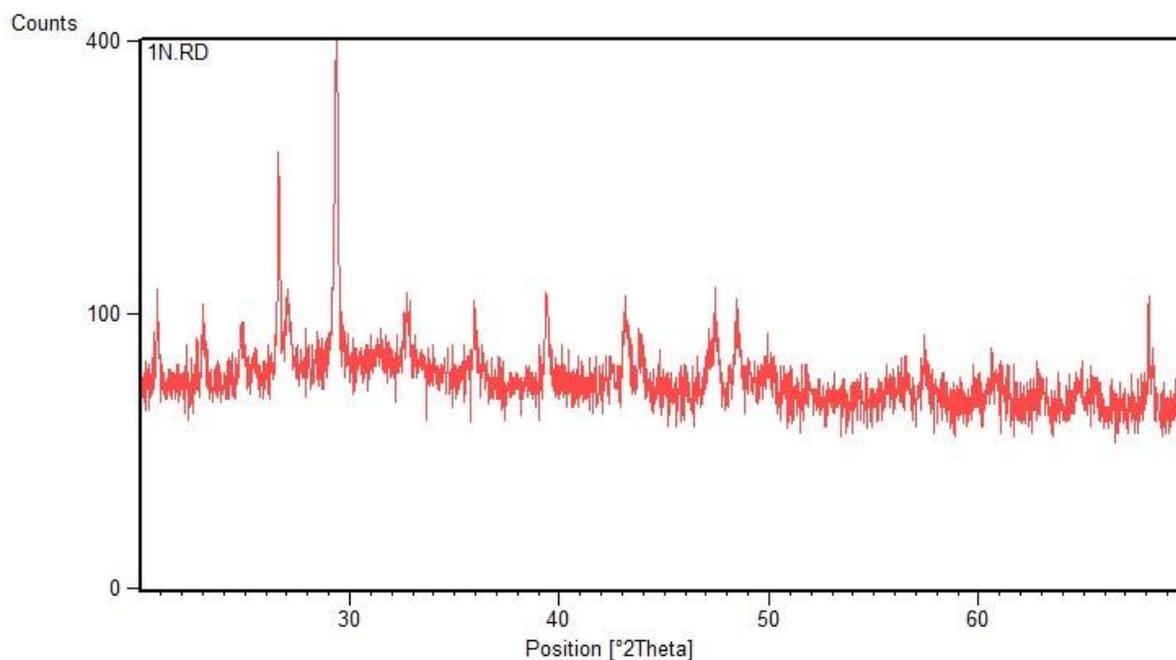


Figure 8: X-ray diffractogram for activated carbon from sludge

5.9 Scanning electron microscope analysis:

The sample of activated carbon produced out of the best operating conditions like 2.0M $ZnCl_2$ activating solution, impregnation time of 20 h, activation temperature of 600 C for 1 h, was analyzed in a scanning electron microscope. The surface physical morphology of activated carbon was observed by a scanning electron microscopy (SEM) (S-2150, Hitachi High-Technologies Corp., Japan).

SEM photograph shows that wide variety of pores is present in activated carbon along with fibrous structure. $ZnCl_2$ and NaOH impregnated carbon consists of more canals like structure than the untreated carbon. In cases of $ZnCl_2$ and NaOH impregnated activated carbon, surfaces are pitted and fragmented. Those imperfections are not seen in case of untreated sludge.

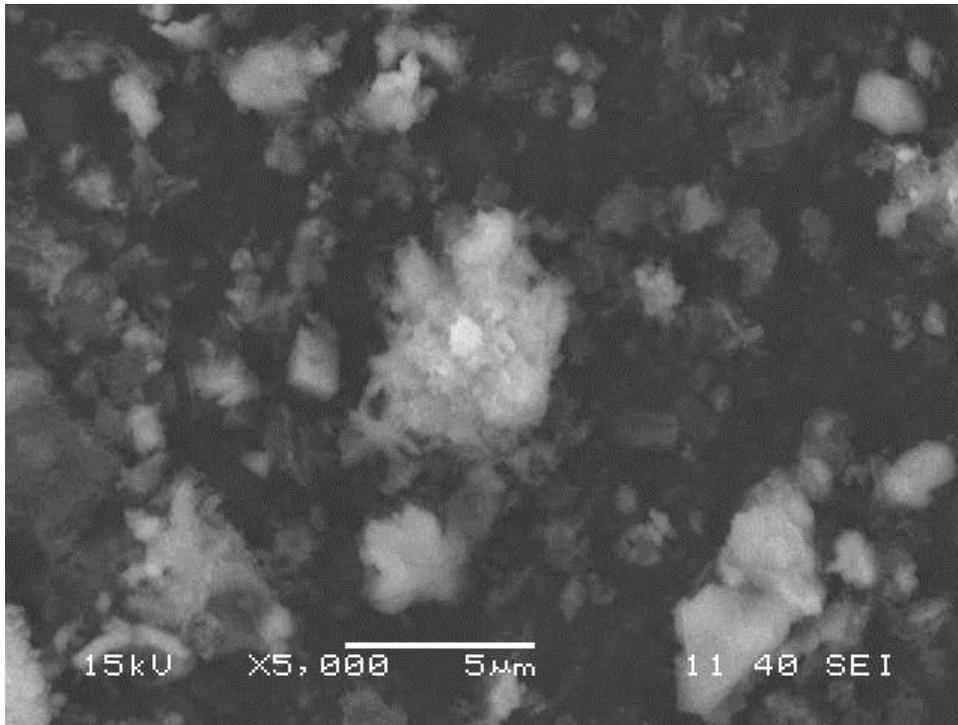


Figure 8: SEM image of untreated sludge at 5000 times magnification.

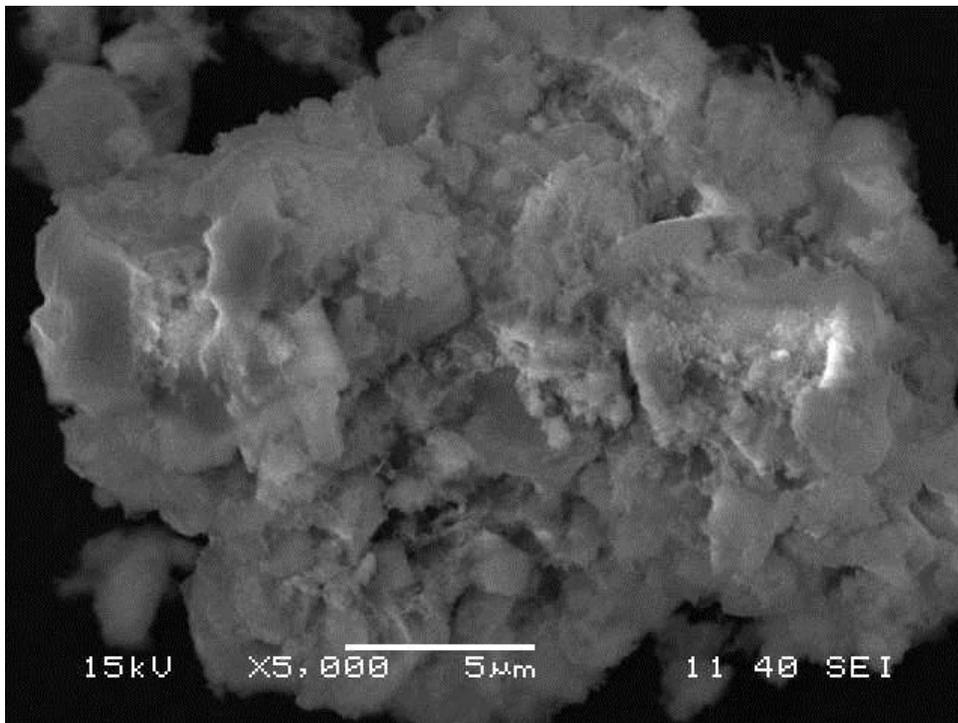


Figure 9: SEM image of KOH activated carbon at 5000 times magnification.

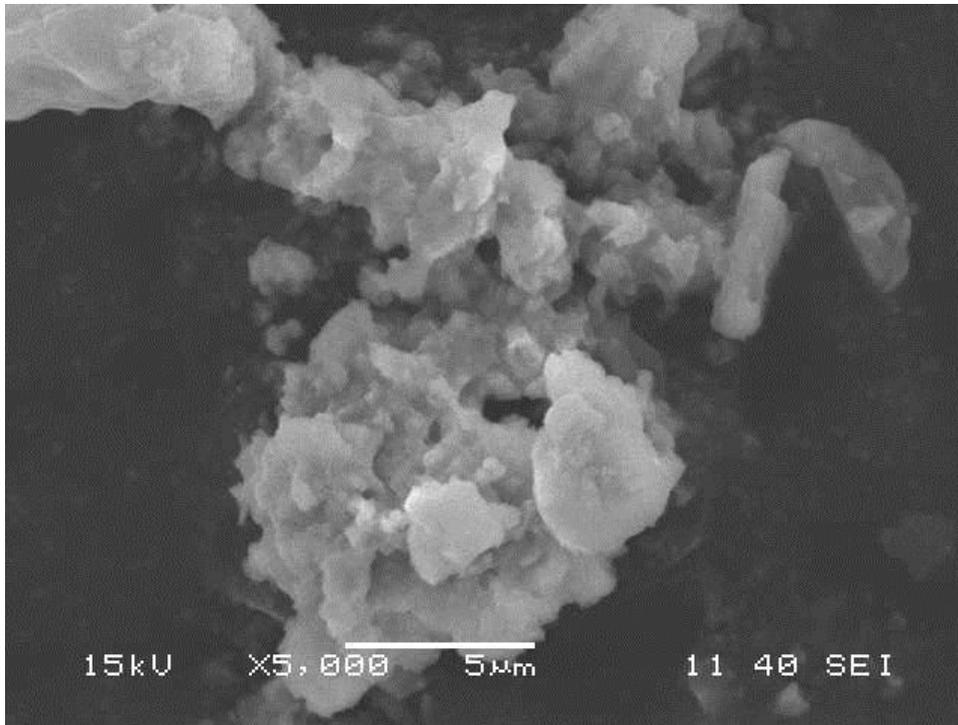


Figure 10: SEM image of ZnCl₂ activated carbon at 5000 times magnification.

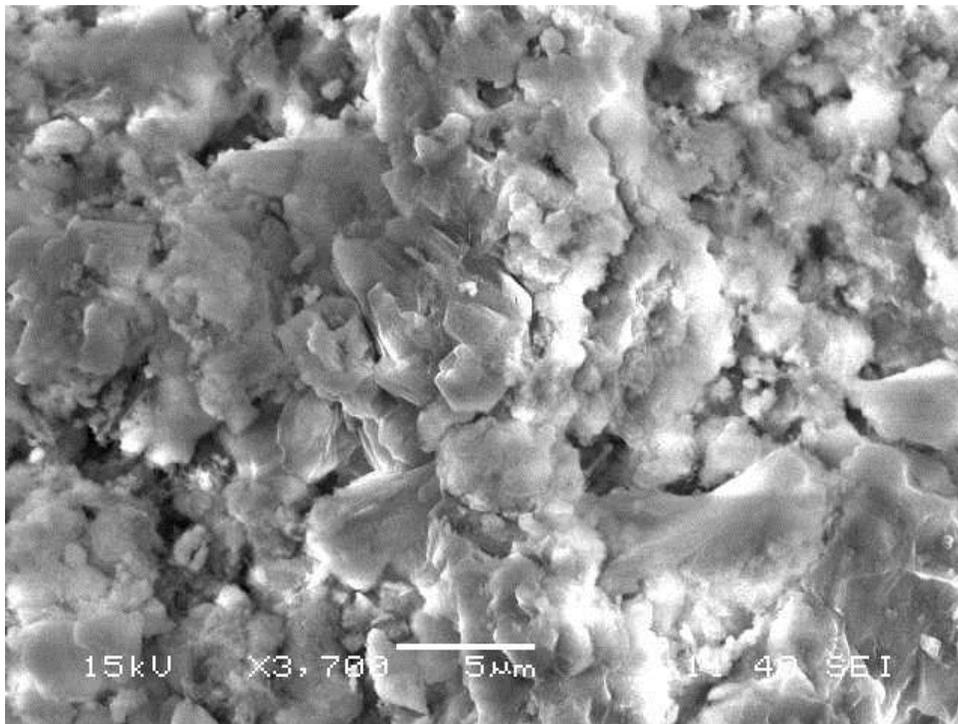


Figure 11: SEM image of untreated sludge at 3700 times magnification

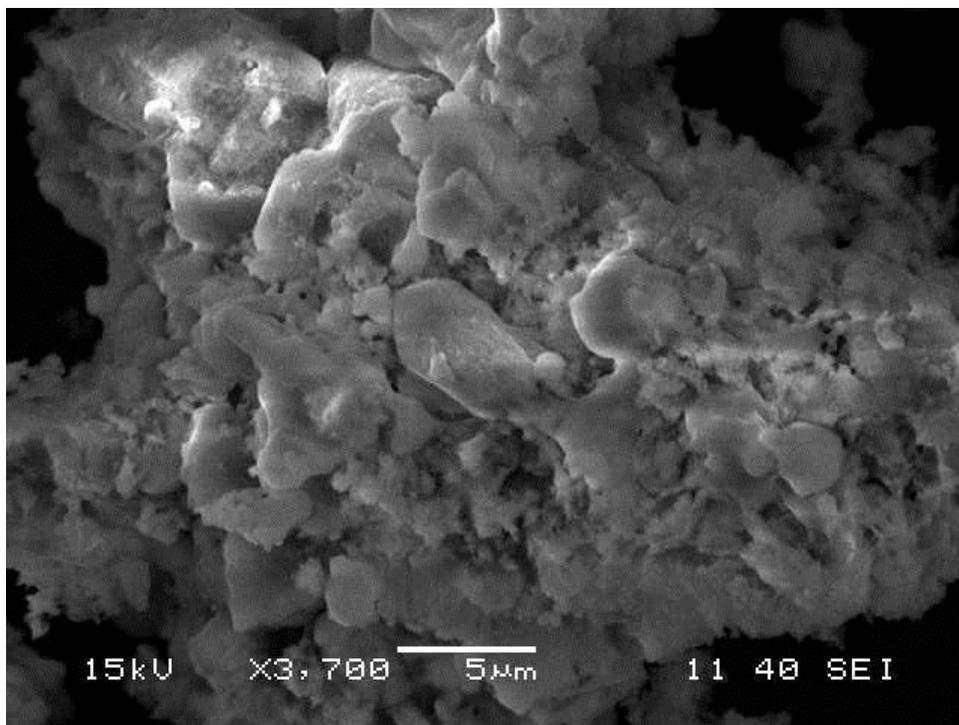


Figure 12 : SEM image of KOH treated activated carbon at 3700 times magnification.

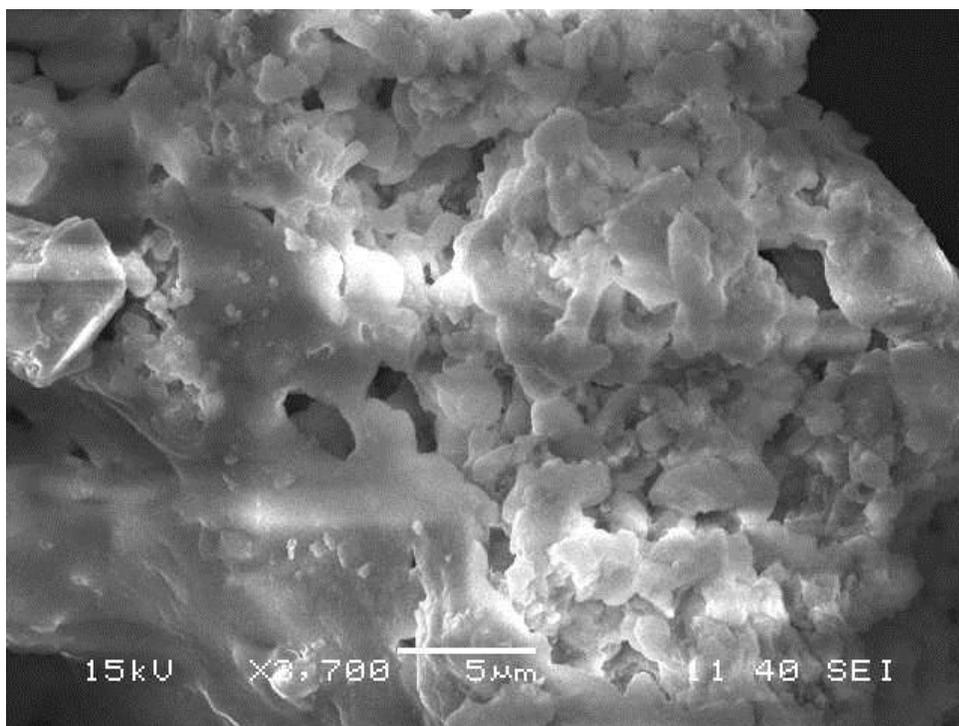


Figure 13: SEM image of ZnCl₂ activated carbon at 3700 times magnification.

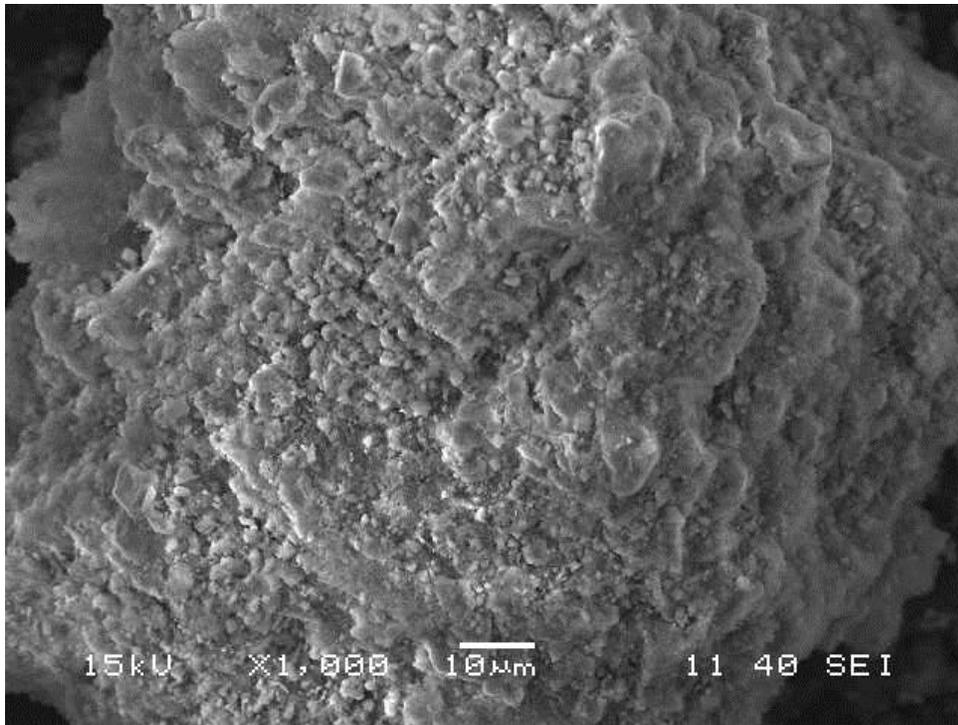


Figure 14: SEM image of untreated sludge at 1000 times magnification.

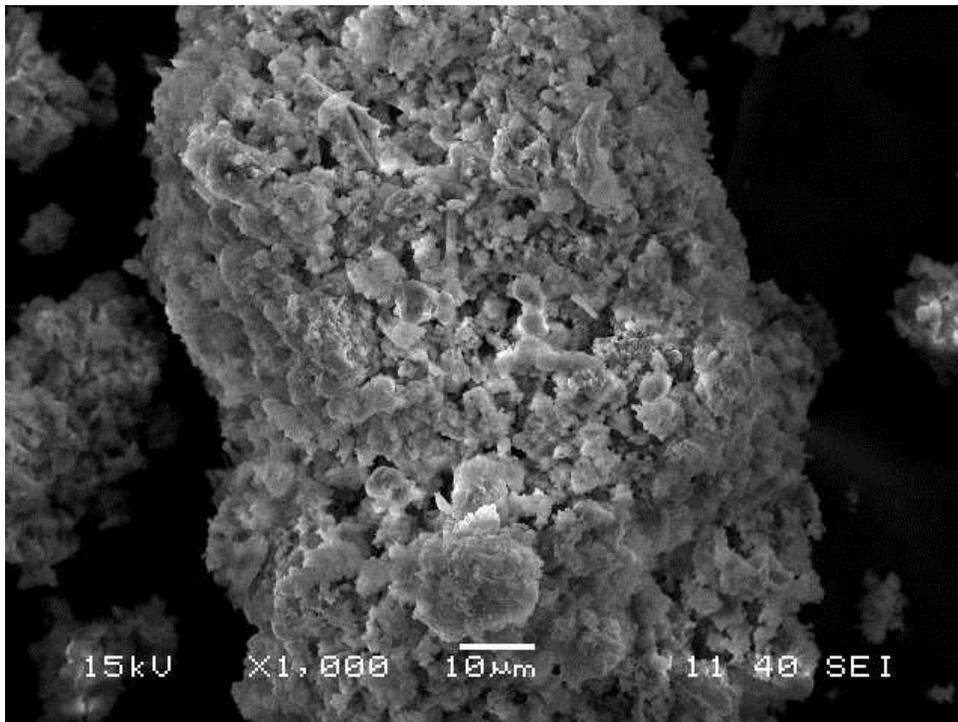


Figure 15: SEM image of KOH treated sludge at 1000 times magnification.

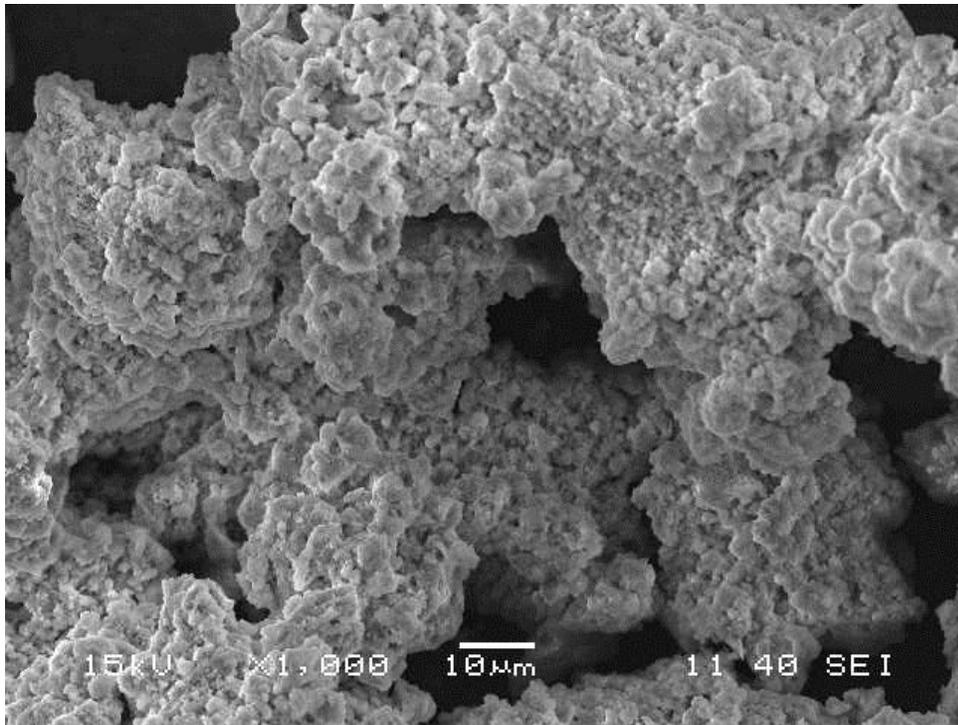


Figure 16: SEM image of ZnCl₂ activated carbon at 1000 times magnification.

CHAPTER 6

CONCLUSIONS

6. Conclusions:

The results of this study show that it is feasible to prepare activated carbons with relatively high surface areas and pore volumes from paper sludge by direct chemical activation. An activation with ZnCl_2 produced activated carbons with better developed porosities than with KOH or KCl. The iodine value of the activated carbon product increased with concentration of ZnCl_2 solution (up to 2 N). As the impregnation time increased, the iodine value rose steeply, reaching a maximum value of 764.8mg/gm after 20 h. The iodine value also increased with activation temperature up to 600 C, beyond which it gradually decreased, presumably due to excessive carbonization. While prolonging the activation time, the iodine value of ZnCl_2 -activated carbon increased and then reached its maximum at 1 h. A longer activation time could induce negative effect on the carbon structure, and, thus, decrease the iodine value. In order to have a high surface area carbon and to minimize the energetic cost of the process, the following optimal conditions, 2.0M ZnCl_2 activating solution, impregnation time of 20 h, activation temperature of 600 C for 1 h were achieved. Under these conditions, activated carbon with a relatively high specific surface area of 737.6m² /g and high iodine value of 764.8mg/ g was produced from paper sludge by direct chemical activation. The porosity of the product was comparable with that of commercially achieved carbon. The sludge-based activated carbon had a mean pore diameter of 6.72 nm, and its total pore volume and micro pore volume were 0.19 and 0.15cm³ /g, respectively, indicating its micro porous and meso porous character.

CHAPTER 7

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