CHARACTERIZATION OF MICROWAVE ACTIVATED CARBON DERIVED FROM THE MIXTURE OF PALM KERNEL AND COCONUT SHELLS

BY

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DECLARATION

I declare that the work in the dissertation entitled “Characterization of microwave activated carbon derived from the mixture of palm kernel and coconut shells” has been performed by me in the Department of Physics, Ahmadu Bello University Zaria, under the supervision of Dr. U. Ahmadu and Dr. U. Sadiq.

The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this work was previously presented for another degree or diploma at any University.

---------- Date----------

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CERTIFICATION

The dissertation entitled “Characterization of microwave activated carbon derived from the mixture of palm kernel and coconut shells” by Egila, Ezekiel Friday with Registration number M.Sc/Sci/3086/2011-2012 meets the regulations governing the award of Masters of Science degree in Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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ABSTRACT

Palm Kernel Shell and Coconut Shell were utilized for the preparation of activated Carbon (AC) by microwave assisted NaCl/$CaCl_2$ chemical activation at microwave radiation power of 700W and radiation time of 20 minutes. The activated carbon Samples were characterized by, Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-,Ray Spectroscopy, X- Ray Diffraction (XRD), moisture content, ash content and adsorption study.

The moisture content in all the samples fall within the acceptable range of less than 70%, according to Tierney *et al.*,2006, which indicates that the adsorption of moisture by the samples is also less. Among the activated carbon samples, sample E has the least moisture content of 6.50 % and an ash content of 3.66%, which suggests that sample E is very viable for adsorption.

The adsorptive properties of the AC samples were quantified using methylene blue (MB), as a model adsorbate. Results showed that the adsorption capacities of the AC samples for MB fitted well in the Langmuir model of adsorption with a maximum adsorption capacity of 333.3mg/g.The adsorption capacity was influenced by theporosity of activated carbon of which the development of the porosity of activated carbon was affected by the Microwave power and the presence of activating agents for impregnation.

In SEM, Sample E gives a clearer pore structure, having more volume of pores and better pore structures with little agglomeration, making it more viable for adsorption in comparison with the other prepared samples.

In XRD characterization, the presence of irregular patterns of X-Ray diffractograms may be accounted for amorphous state of the samples. A sharp peak, which corresponds to $CaCl_2$,

was observed at 26.5° and also, sharp peaks corresponding to NaCl, were observed at two theta 31.5° and 45.0° in Sample E.The findings revealed the potential use of a blend of Palm Kernel and Coconut Shells derived activated carbon for dyes removal and/or impurities within the size range of 1.5nm from wastewater, in general and for the removal of MB, in particular.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Activated carbon (AC); a tasteless solid and black carbonaceous material, has been regarded as a unique and versatile adsorbent because of its extended surface area, microcrystalline porous structure, high adsorption capacity and high degree of surface reactivity. AC is applied widely in a variety of fields such as food and chemical industries, waste water treatment, solvent recovery, air pollution control and hydrometallurgy for the recovery of gold and silver (Sugumaran*et. al.*, 2012). In recent times, carbon has been one of the magnificent elements which have revolutionized materials science. Carbon provides materials with excellent properties for a large spectrum of industrial applications. From carbon we obtain the strongest fibres (carbon fibres), one of the best solid lubricants (graphite), one of the best electrically conducting materials (graphite electrodes), the best structural material for high temperature tribological application (carbon–carbon composites), one of the best porous gas adsorbers (activated carbon), an essentially non-crystalline impermeable material (vitreous carbon), the hardest material (diamond), and now the most fascinating material, the fullerenes. All these forms are made by meticulously choosing the raw materials and processing conditions(Burchell 1999).

Generally, the raw materials for the production of AC are those with high carbon but low inorganic contents such as wood, lignite, coal, coconut shells, wood (both soft and hard), peat and petroleum based residues. Most carbonaceous materials do have a certain degree of porosity and internal surface area. The internal surface area must be accessible to the passage of a fluid or vapor if a potential for adsorption is to exist. Thus, it is necessary

that an activated carbon has not only a highly developed internal surface but accessibility to that surface via a network of pores of differing diameters. As a generalization, pore diameters are usually categorized as follows: Micropores <20 Angstroms, Mesopores 20 - 5,000 Angstroms, Macro pores >5,000 Angstroms (typically 5000-20000 Angstroms)(Lua and Guo, 2004).

A coconut shell based AC will have a predominance of pores in the micro pore range and these accounts for 95% of the available internal surface area. Such a structure has been found ideal for the adsorption of small molecular weight species and applications involving low contaminant concentrations. In contrast wood and peat based ACs are predominantly of Mesopore or macropore structures and are therefore usually suitable for the adsorption of large molecular species. Thus, it is the micropore structure of an activated carbon that is the effective means of adsorption. (Leimkuehler, 2010).

Microwave heating has been successfully applied for the preparation and regeneration of activated carbon (Foo *et al.,* 2011; Emine *et al.,* 2008). Microwave heating is fundamentally different from the conventional form of heating in which thermal energy reaches the surface of the material by radiant and/or convection and is then transferred to the bulk of the material via conduction. This results in poor crystalline structure and often wider distribution of particle size due to non uniform distribution of heat or thermal energy. But in microwave heating, energy is delivered directly to the material through molecular interaction thus producing uniform heating. This often makes the materials to have finer microstructures with narrow particle size distribution (Barrison *et al.,*2010; Utchariyajit *et al.,* 2010). Also, Conventional thermal heating of activated carbon decreases the adsorption capacity, which is attributed to the adverse changes in the adsorbent physical structure

(Bathen, 2003). In contrast, microwave energy can maintain and or even slightly enhance the adsorbent physical structure to an acceptable level (Alireza *et al.,* 2010). In summary, microwave heating has many advantagesover conventional heating in that microwave energy has no need for heat convection through a fluid, microwave energy does not have any need of direct contact between the microwave heating source and the heated material, it saves time and energy and uniform temperature distribution. Moreover, microwave processing systems are also relatively compact, portable, maintainable and cost effective (Bathen, 2003; Carrott *et al.,* 2001). Since microwaves can penetrate the material and supply energy, heat can be generated throughout the volume of the material resulting in volumetric heating. Volumetric heating means that materials can absorb microwave energy directly and internally and convert it to heat. Also, it is this characteristic that leads to advantages using microwaves to process materials (Thostenson and Chou, 1999; Xiaofeng Wu, 2002). Hence, it is expected that microwave heating will be a viable technology for activating carbon. Studies have shown microwave energy to be a possible method in waste treatment for extracting contaminants and organic solvents from soil (Liu and Yu, 2006) and metals from sludge (Menendez and Inguanzo, 2002), and for processing minerals (Jones et al., 2002) and water purification (Bandosz, 2006). Microwave (MW) radiation has also been used for the production of activated carbon (Nabais *et al.,* 2004). Studies have shown that granular activated carbon (GAC) can absorb MW radiation, leading to rapid heating (Guo *et al.,* 2000). So far, there are relatively few studies in this field where activity can be controlled by altering the proportion of raw material to activating agent. Menéndez *et al.,(*1999) and Liu *et al.*,(2010) have reported the surface modification of activated carbon and activated carbon fiber by means of microwave heating. In this study, two kinds of activated carbons (Palm

kernel shell-based and coconut shell-based) using a microwave device under an input power was used instead of the conventional heating system. The effects of microwave heating on the activated carbons were characterized and analyzed.

1.2 REVIEW OF PREVIOUS WORK

A number of researches have been reported in the literature using microwave assistance of different activated carbons.

Alireza*et al.*, (2010) examined the impact of microwave irradiation on the regeneration of granular activated carbon (GAC) exposed to toluene vapor. The regeneration efficiency was more than 95% after 5 cycles at higher power levels. The GAC surface area was increased from 1150 m^2 /g to 1185 m^2 /g over regeneration cycles. They concluded that GAC could be reused after repeated regeneration cycles under microwave irradiation while maintaining its original adsorption capacity and physical properties.

Foo *et al.*, (2011) studied the Preparation and characterization of activated carbon from melon seed hull by microwave-induced NaOH activation. In their work, melon seed hull (MS), an industrial effluent abundantly available from the melon seed oil processing plants was utilized as a feedstock for preparation of activated carbon (Melon Seed Activated Carbon, MSAC) by microwave assisted NaOH chemical activation. MSAC was characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, elemental analysis, and nitrogen adsorption–desorption study. The findings revealed the potential use of melon seed derived activated carbon for cationic and anionic dyes removal.

Liqiang Zhang*et al.*, (2013) studied the modification of activated carbon by means of microwave heating and its effects on the pore texture and surface chemistry. The results showed that microwave heating is an effective means of activatedcarbon modification. The temperature of activated carbon increased rapidly with increasing input power under microwave heating and thengradual increase to a quasi-stationary temperature. The pore texture of activated carbon changes slightly aftermicrowave treatment and the two activated carbons still keep rich pore structure.

In this work, a mixture of coconut shell and palm kernel shell, impregnated with varying concentrations of the activating agents (NaCl and $CaCl_2$), was used to produce activated carbon via the aid of microwave heating. The produced activated carbon was used to examine its potentiality for water treatment applications.

1.3 STATEMENT OF THE PROBLEM

Addressing the deterioration of water quality in developing countries, where an estimated one billion people lack access to potable quality water, is a primary motivating factor for many community development efforts and is a key component of the Millennium Development Goals. Water quality improvements inspired by these goals are currently focused on reducing diarrheal illnesses and, hence, are focused on biological contamination and related pathogen removal. These water quality improvements are commonly achieved by point of use (POU) treatment systems in developing countries. POU water treatment alternatives have been introduced and successfully implemented within impoverished areas, primarily where nonprofit organizations have taken greater notice and where governments have emphasized the need for improved water quality. Despite the efficiency of these

systems at removing biological contaminants, they lack the ability to effectively remove dissolved organic impurities such as pesticides. Additional treatment is required in areas where such contaminants are prevalent.

1.4 JUSTIFICATION OF RESEARCH WORK

This study has been initiated to identify an inexpensive option to remove impurities from drinking water. In view of the aforementioned limitation, the main goal of this study is to enhance the purification of water via the use of local agricultural waste byproducts to produce a low-tech, chemically activated carbon that could be used in conjunction with existing POU technologies or as a stand-alone treatment option.

1.5 AIM AND OBJECTIVES OF THE RESEARCH

The aim of this research work is to produce activated carbon from a mixture of coconut shells and palm kernel shells with varying concentrations of activating agents employing Microwave-assisted route and to explore its potentiality for water treatment. The following objectives will guide in achieving the aforementioned aim:

i. To evaluate the activation power and time for the production of activated carbon from the mixture of the coconut shells and palm kernel shells.

ii. To study the structure of the activated carbon produced using Scanning Electron Microscopy.

iii To characterize the activated carbon produced in terms of elemental composition, adsorption capacity, surface functionality, pore size and phase composition using:

(a) XRD, (b) SEM and (c) EDS

1.6 SCOPE OF THE RESEARCH

In this research, parameters of the activated carbon produced (i.e. elemental analysis, adsorption capacity, surface functionality and pore size) will be evaluated using X -Ray Diffractometer (XRD), Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-Ray Spectroscope (EDS).

CHAPTER TWO

LITERATURE REVIEW

2.1. INTRODUCTION

Activated carbon forms a large and important class of porous solids, which have found a wide range of technological applications. As such, the porous structures of these materials and their adsorption of gases, vapors, and liquids have been extensively studied. In this section the micro structural and porous properties of the principal classes of activated carbon are reviewed. It is outside the scope of this contribution to consider the very many industrial applications and processes of activated carbon.

2.1.1 Definition of Activated Carbon

Suguraman (2012) defined Activated carbon (AC) as a tasteless, microcrystalline, graphitic form of black carbonaceous solid material with a porous structure. The main features common to all AC are that they are graphite like planes which show varying degrees of disorientation and the resulting spaces between these planes which constitute porosity. Benaddi*et al.,* (2000) also stated that AC is predominantly an amorphous solid with a large internal surface area and pore volume. Cokes, chars and activated carbon are frequently termed amorphous carbon.

From these definitions, it can be summarized that AC is a black, amorphous solid containing major portions of fixed carbon content and other materials such as ash, water vapor and volatile matters in smaller percentage. Besides that, AC also contains physical characteristics such as internal surface area and pore volume. The large surface area results

in a high capacity for adsorbing chemicals from gases or liquids. The adsorptive property stems from the extensive internal pore structure that develops during the activation process.

2.2 CHARACTERIZATION OF ACTIVATED CARBON

Characterization for activated carbon (AC) is very important in order to classify AC for specific uses. Basically, LuaandGuo (2004) mentioned that the characteristics of activated carbon depend on the physical and chemical properties of the raw materials as well as activation method used.

Physical properties of AC, such as ash content and moisture content can affect the use of a granular AC and render them either suitable or unsuitable for specific applications. While the specific surface area of activated carbon and surface chemistry is classified as chemical properties, such surface chemistry (surface functional groups) could be characterized using the Fourier Transform InfraRed (FTIR). Furthermore, the porous structure of activated carbon also can be characterized by various techniques such as Scanning Electron Microscopy (SEM), adsorption of gases(N_2, Ar, Kr, CO_2) or vapours (benzene, water), and Transmission Electron Microscopy (TEM).

2.2.1 Moisture Content

Activated carbon is generally priced on a moisture free basis, although occasionally some moisture content is stipulated, e.g., 3, 8, 10%. Unless packaged in airtight containers, some activated carbons when stored under humid conditions will adsorb considerable moisture over a period of 1- 2 months. They may adsorb as much as 25 to 30% moisture and still appear dry. For many purposes, this moisture content does not affect the adsorptive power

until the relative humidity exceeds 75%, but obviously it dilutes the carbon (Tierney *et al*., 2006).

The moisture content can be obtained by;

$$\% \text{ moisturecontent} = \frac{(b-c)g \times 100}{1.0g} \quad (2.1)$$

Where

Mass of crucibles + original Sample = (b)g
Mass of crucible + sample after drying = (c)g
Moisture content = (b – c)g

2.2.2 Ash content

The ash content of a carbon is the residue that remains when the carbonaceous material is burnt off. As activated carbon contain inorganic constituents derived from the source materials and from activating agents added during manufacture, the total amount of inorganic constituents will vary from one grade of carbon to another. The inorganic constituents in a carbon are usually reported as being in the form in which they appear when the carbon is ashed. Ash content can lead to increased hydrophilicity (ability to dissolve in water) and can have catalytic effects, causing restructuring process during regeneration of used activated carbon. The % ash content (dry basis) would be calculated from the equation below;

$$\text{Ash\%} = \frac{F-G}{B-G} \text{X } 100\% \quad (2.2)$$

Where:

Mass of crucible + ashed sample (g) = F

Mass of crucible + dried sample (g) = B

Mass of empty crucible (g) = G

(Rengaraj *et. al.*, 2002)

2.2.3 Pore structure

The word pore comes from the Greek word, meaning a passage. In this sense, a pore is a class of void which is connected to the external surface of a solid and will allow the passage of fluids into, out of, or through a material. Hu *et. al.*, (2001) claim that, in the scientific literature on porous solids the terms ‘open pore’ and ‘closed pore’ are used. Examples of different pore types are shown schematically in Figure 2.1

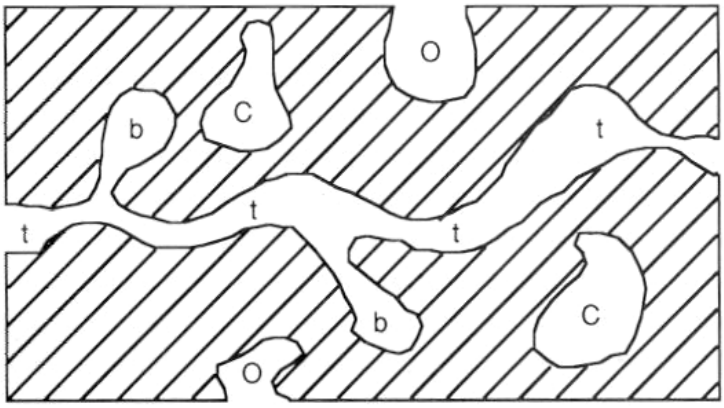


Figure 2.1 Different types of porosity in a porous solid Hu *et. al.*, (2001) ;

O-open pores; C- closed pores; t-transport pores; b-blind pores.

Transport pores are those pores in which a concentration gradient exists during steady state or time-independent fluid flow through the material. Blind pores are connected to transport pores by a single opening so that in them concentration gradients and hence fluid flow only

occur during unsteady state or time independent flow. Differences in pore sizes affect the capacity for molecules of different shapes and sizes, and this is one of the criteria by which carbons are selected for a specific application. Porosity is classified by IUPAC into three different groups of pore sizes (Lua and Guo, 2004):

i. Micropores- width less than 2nm

ii. Mesopores- width between 2nm and 50nm

iii. Macropores- width greater than 50nm

The schematic of internal pores structure in activated carbon is shown in Figure 2.2 below.

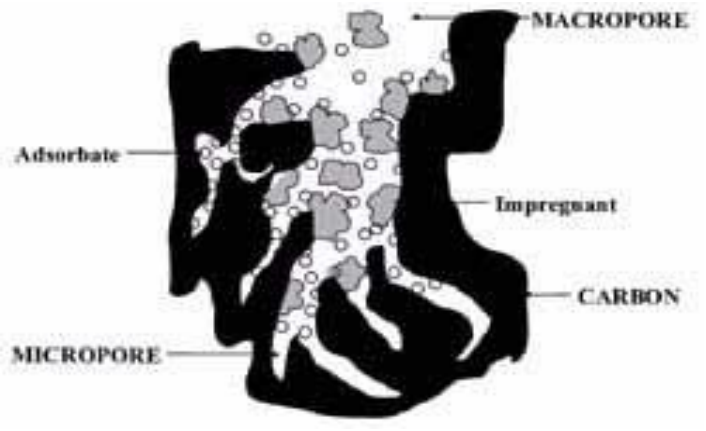
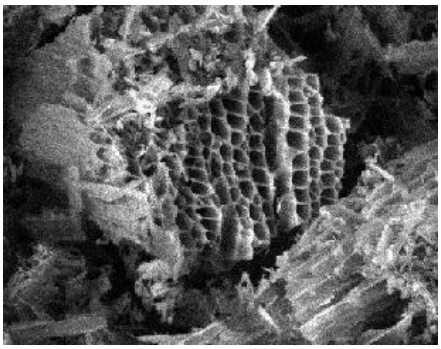


Figure 2.2 Schematic of internal pore structure of activated carbon

Micropores are formed in the interlayer spacing with widths in the range 0.34- 0.8nm. It is the micropores in activated carbon which have the greatest influence upon gas adsorption, while macropores and mesopores are important in transport of fluids to and from the micropores.

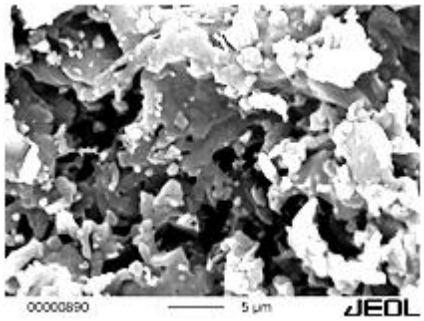
Adsorption takes place in micropores and mesopores with macropores acting as transport channels. In adsorption from the gas phase, mainly microporous carbon is used whereas

mesoporous carbon is applied in liquid phase processes (Benaddi *et al.,* 2000). Beside their significant contribution to adsorption, mesopores also serve as the main transport arteries for this adsorbate (Hu *et al.,* 2001).

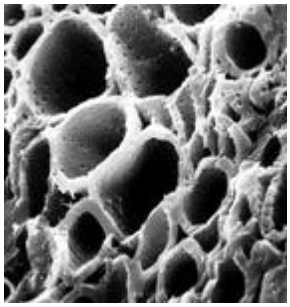


(a)

(b)



(c)



(d)

Figure 2.3 SEM shows different shape of pores depending on types of raw materials.

(a) Coal (http://www.air-purifier_home.com/images/2-ccoall.jpg),

(b) Wood (http://www. Yahoo.com/images/pore carbon/activated carbon wood.jpg)

(c) Husk (http://www. Yahoo.com/images/pore carbon/husk.jpg)

(d) Coconut (http://www.lunor.ch/english/nbcfilters.html)

The distribution of pores in activated carbons can vary significantly, depending on the raw material. Figure 2.3 shows the different shape of pore with different raw materials. The pore size distribution also affects the efficiency and selectivity of adsorption. A consideration of the dimensions of some pollutants shows that activated carbon can feasibly be used to remove many of the impurities occurring in water (Lua and Guo, 2004). The small organic molecules with low solubility have sizes in the range 0.6 to 0.8 nm and can be adsorbed in micropores while large compounds such as color molecules and humid acids have dimensions around 1.5 to 3.0 nm that will favor their adsorption in mesopores. Table 2.1 showed the minimum pore diameter for adsorbate. (McEnaney*et al.,* 1995)

Table 2.1 Minimum pore diameter for adsorbate

Adsorbate	Minimum Pore, Diameter, Å
Iodine	10
Potassium permanganate	10
Methylene Blue	15
Erythrosine Red	19
Molasses	28

2.2.4 The microstructure of activated carbon

Activated carbon, relatively known as amorphous carbon, show a very disordered microcrystalline structure in which graphitic microcrystals are randomly oriented.

One of the examples of microporous structure for activated carbon is shown in figure 2.4. Typically, in non graphitizing carbons heated to 900°C the interlayer spacing are separated by small stacks of two or three carbon layer planes. Thus, micropores are an inherent feature of the microstructure of activated carbon. (McEnaney, 1995)

Figure 2.4 A model for the microstructure of a microporous carbon (McEnaney*et al.,* 1995)

Another feature of the microstructure is constrictions in the microporous network that control access to much of the micropore space. Also, entrances to micropores may be blocked by functional groups attached to the edges of layer planes and by carbon deposits formed by thermal cracking of volatiles released during carbonization. Thus, the micropores in activated carbons are incorporated into an aperture cavity network. Constrictions and blockages in the microporous network cause activated diffusion effects at low adsorption temperatures when the adsorptive has insufficient kinetic energy to penetrate the pore space completely (McEnaney *et. al.,* 1995).

2.3CHARATERIZATION TECHNIQUES

Among the several characterization techniques, X- Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDXS) and Fourier

Transform Infrared Spectroscopy (FTIR) are the four important techniques. Others like Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and Differential Thermal Analysis (DTA) are also employed for further characterization purposes.

2.3.1 X- Ray Diffraction

X-Ray diffraction is a useful tool to obtain structural information of crystals. It is used to measure the average spacing between layers or rows of atoms, determine the orientation of a single crystal or grain, find the crystal structure of an unknown material and measure the size, shape and internal stress of small crystalline regions.

In an X-ray diffraction measurement, a crystal is mounted on a goniometer and gradually rotated while being bombarded with X-rays, producing a diffraction pattern of regularly spaced spots known as *reflections*. The two-dimensional images taken at different rotations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with chemical data known for the sample. Poor resolution (fuzziness) or even errors may result if the crystals are too small, or not uniform enough in their internal makeup (Bras *et. al.*, 2005).

2.3.1.1X-Rays Scattering by Crystalline Solids

The knowledge of X-rays and that of the geometry of crystals must be combined together, in order to get a clear picture of the phenomenon of X-ray diffraction. Diffraction is essentially a scattering phenomenon and not involving any new kind of interaction between X-rays and

atoms. The usefulness of X-ray diffraction as a diagnostic tool for material characterization lies in its ability to distinguish crystalline materials from amorphous one. The resolution of crystalline structure of materials by X-rays is related to their small wavelength (~0.5nm-about the atomic spacing) compared to visible light (600nm) (Weller, 2006).

All crystalline materials adopt, in all solid state, a regular distribution of atoms or ions in space. The simplest portion of the structure, which is repeated by translation, and shows its full symmetry, is called the unit cell. When a monochromatic beam of X-rays strikes a crystal, the atomic planes of the crystal act in a similar manner to diffraction grating, and the X-rays exciting the specimen exhibit constructive and destructive interference according to the experimental geometry. A study of the X-rays scattered by crystalline materials provides a wealth of structural information (Cullity *et al.*, 2001).

Atoms scatter incident X-rays in all directions and in some of these directions, the scattered beams will be completely in phase and so reinforce each other to form diffracted beams. In order to get a clear notion of phase relations, the scattering of X- Rays from crystalline solids can be demonstrated by consideration of the diffraction from points as a set of lattice planes. Considering fig 2.5 below, the scattering of the impinging X-ray beam from points B and G in neighbouring planes will produce, in phase, diffracted X-ray beams (constructive interference) if additional distance travelled by the X-ray photon scattered from E is an integral number of wavelengths. This path difference GE+ EH will depend on the lattice spacing or $d_{hkl,}$

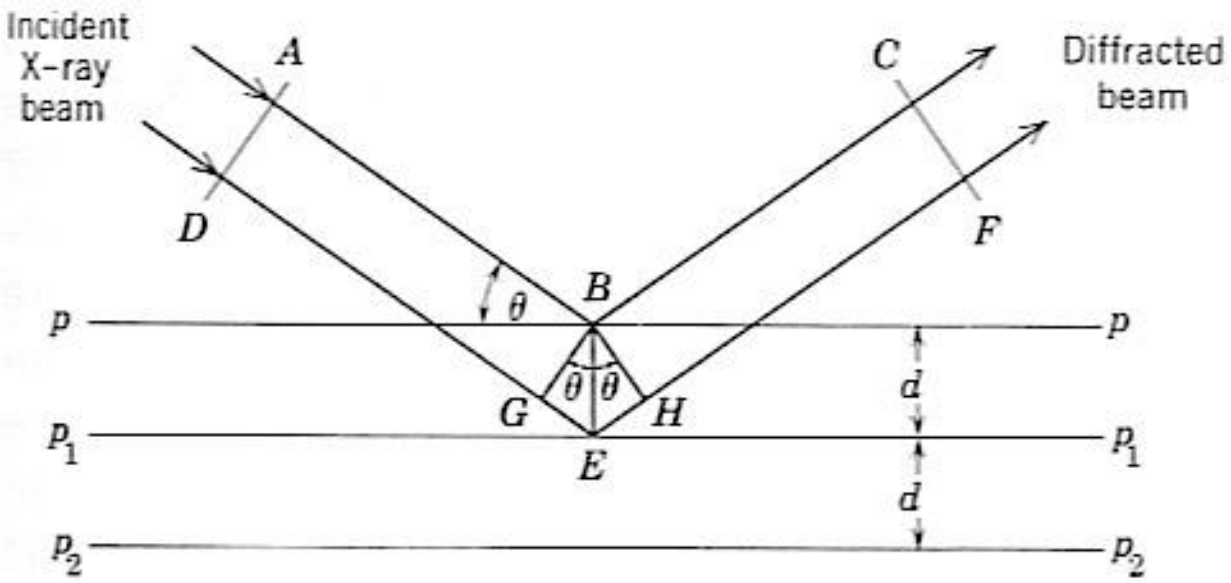


Figure 2.5 Scattering of an X-ray beam by a crystal (Callister, 1997)

Where hkl are Miller indices for planes under consideration, and will also be related to the angle of indices of the X- ray beam, θ. For an integral wavelength, the following relationship between θ and d_{hkl} can be obtained as

$$\text{Path difference} = GE + EH = 2d_{hkl} \sin\theta = n\lambda \quad (2.8)$$

here n is an integer, λ is the X- ray wavelength. We may identify the distance between planes with indices *hkl*(for cubic materials with lattice parameter a) as;

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2.9)$$

Equation (2.8) is known as Bragg's law. (Cullity *et al.*, 2001)

2.3.1.2X- Ray Diffraction Methods

Diffraction can occur whenever Bragg's law ($\lambda = 2d \sin \theta$) is satisfied. This equation puts very stringent conditions λ and θ for any given crystal. With monochromatic radiation, an arbitrary setting of a single crystal in a beam of X- rays will not in general, put any diffracted beams. Some way of satisfying Bragg's law must be devised, and this can be done by continuously varying either λ or θ during the experiment. The ways in which these qualities are varied distinguish the three main diffraction methods (Callister, 1997).

The Laue method was the first method ever used, and it reproduces von Laue's original experiment. In this experiment, a beam of white radiation, the continuous spectrum from an X-ray tube falls on a single crystal. The Bragg angle θ is therefore fixed for every set of planes in the crystal, and each set selects and diffracts that particular wavelength which satisfies Bragg's law for the particular values of d and θ involved. Each diffracted beam thus has a different wavelength (Cullity *etal.*, 2001).

In the rotating crystal method, a single crystal is mounted with one of its axes, or some important crystallographic direction, normal to a monochromatic X-ray beam. A cylindrical film is placed around it and the crystal is rotated about the chosen direction, the axis of the film coinciding with the axis of rotation of the crystal. As the crystal rotates, a particular set of lattice planes will, for an instant, make a correct Bragg angle for diffraction of the monochromatic incident beam, and at that instant, a diffracted beam will be formed. (Cullity *etal.*, 2001).

In the powder method, the crystal to be examined is reduced to a very fine powder or already is in the form of loose or consolidated microscopic grains. The sample in a suitable holder is placed in a beam of monochromatic X- rays. Each particle of the powder is a tiny

crystal or assemblage of smaller crystals, oriented at random with respect to the incident beam. Just by chance, some of the crystals will be correctly oriented so that their (100) planes, for example, can diffract the incident beam. Other crystals will be correctly oriented for 110 reflections, and so on. The result is thatevery set of lattice planes will be capable of diffraction. The mass of powder is equivalent, in fact, to a single crystal rotatetd, not about one axis, but aboutall possible axes. (Cullity *etal.,* 2001).

When properly employed, powder diffraction can yield a great deal of structural information about the material under investigation. The method is thus eminently suited for materials work, since crystals are not always available and such materials as polycrystalline wire, sheet, rod, polymeric fibres, may be examined non- destructively without any special preparation. (Poole *et al.,* 2003).

2.3.1.3 X-Ray Diffractometer and its application

An X- ray Diffractometer is an instrument for studying crystalline and non crystalline materials by measurements of the way in which they diffract (scatter) X-rays of known wavelength. In the X-ray Diffractometer, the intensity of the diffracted beam is measured directly by an electronic X-ray detector. The detector converts the incoming X-rays to into surges or pulses of electric current, which are fed into various electronic components including computers, for processing. The electronics counts the number of current pulses per unit time, and this number is directly proportional to the intensity of the X-ray beam entering the detector (Poole *et al.,* 2003).

Basically, an X-ray Diffractometer is designed somewhat like the Hull/ Debye camera, except that a movable detector replaces the strip of film. In both instruments, essentially,

monochromatic radiation is used and the X-ray detector or film is placed on the circumference of a circle or on the powder specimen. The essential features of an X-ray Diffractometer are shown in Figure (2.6).

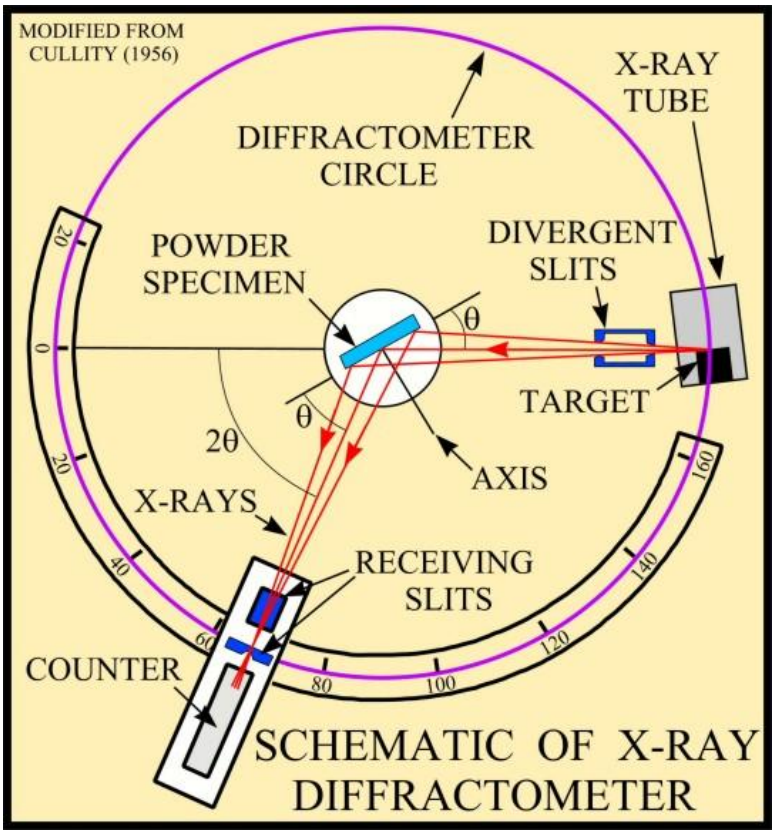


Figure 2.6: A schematic diagram of the X-ray Diffractometer (Cullity *et al.*, 2001).

A powder specimen, in the form of a flat plate is supported on a table, which can be rotated about an axis perpendicular to the the plane of the drawing. The X-ray source is normal to the plane of the drawing and therefore, parallel to the Diffractometer axis. X-rays diverge from this source and are diffracted by the specimen to form a convergent diffracted beam which comes to a focus at the slit and then enters the detector. The slits define and collimate

the incident and diffracted beams. The monochromator or filter is usually placed in a special holder in the diffracted, rather than the incident beam. A monochromator in the diffracted beam not only serves to suppress k□ but also decreases background radiation originating in the specimen (Cullity *et al.,* 2001).

The receiving slits and detector are supported on the carriage, which may be rotated about the axis and whose angular position 2θ may be read on the graduated scale. The carriage and table are mechanically coupled so that a rotation of the detector through 2x degree is automatically accompanied by rotation of the specimen through x degrees. This coupling ensures that the angle of incidence on the flat specimen always equals the exit angle, and both equal to half the total angle of diffraction, an arrangement necessary to preserve focusing conditions. In older instruments, the detector may be power driven at a constant velocity about the Diffractometer axis or moved by hand to any desired angular position. Modern automated Diffractometer generally collect data with the detector and sample set at a large number of fixed angles spaced by an angular increment on the order of 0.010; the length of time counted and the size of the angular increment are controlled through software (Cullity *et al.,* 2001).

2.3.2 Scanning Electron Microscopy (SEM)

Development of strategies to grow crystals of controllable structure, size, morphology and superstructures of pre-defined organizational order is an important goal in crystal engineering with tremendous implications in the ceramic industry (Fathers *et al.,* 1973).

Scanning Electron Microscopy (SEM) provides important information about topography, morphology, grain boundary, grain size, shape, distribution, voids, pores, flaws, cracks and homogeneity of the materials. SEM is associated with a high magnification and resolved power, therefore, heterogeneous organic and inorganic bulk specimens can be examined on a micrometer and nanometer scale. It gives a three dimensional appearance of the specimen image because of the large depth of the field.

In SEM, the area to be examined or the micro volume to be analyzed is irradiated with finely focused electron beam, which may be swept in a raster across the surface of the specimen to form images or may be static to obtain an analysis at one position. The type of signals produced. From the interaction of the electron beam with the specimen include secondary electrons, back scattered electrons, Characteristic X-ray and other photons of various energies. These signals are obtained from specific emission volumes within the specimen like surface topography, crystallography, composition, induced conductivity, magnetic and electric fields, voltage and contrast information (Grundy *et al.*,2003). The most important advantage of SEM is its excellent resolution when compared with the optical microscope. Vastly increased depth of focus in the SEM is also of special value. The SEM accepts much bigger specimens and offers more maneuverability with regard to their positioning.

2.3.2.1 The Scanning Electron Microscope

The microscope is essentially a probe forming instrument, consisting of two lenses. The electron gun works within the range of 0- 50kv while the specimen is maintained at the earth potential. Each of the lenses performs a condensing action and successively demagnifies the

beam source (size d_0~ 50μm)down to a focused spot size d at the specimen. The relation between d and $d_0$is

$$d = M_1M_2d_0 \quad (2.10)$$

where $M_1$and $M_2$are the demagnifications of the lenses. Strictly speaking, equation (3.0) is only valid in the absence of aberrations when d becomes the Gaussian spot size (Valdre, 1971). Actually, because aberration do exist, the spot size on the specimen is somewhat larger than d. $M_1$and $M_2$are controlled by the excitation currents and the latter also depends on the working distance i.e. the distance between the objective lens and the specimen. The electron beam falling on the specimen is often termed "probe" and carries a current typically of 100pA. The schematic diagram of the electron optical column of the SEM is given in figure 2.7. Although two lenses are depicted, but the number is by no means a standard.

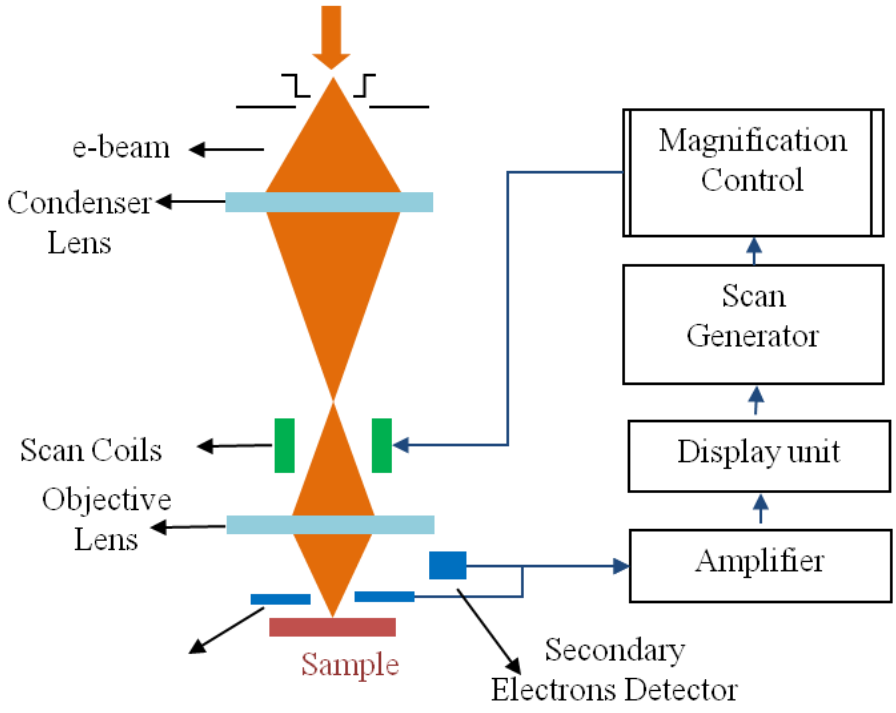


Figure 2.7: A schematic diagram of the scanning electron microscope(Fathers *et al.*, 1973).

The final lens is sometimes called the objective lens, despite its demagnifying action, possibly, because it is used to focus the specimen. The working distance and the final lens aperture diameter, have a strong control on the divergence of the beam, which in turn determines the current density at the specimen. Commonly found values for the final lens aperture diameter are 50, 100 and 200μm.

The microscope gets its name from the action of two sets of scanning coils incorporated near the final lens. In the most common arrangement, when energized by a suitable scan generator, the coil causes the beam to pivot about the centre of the final lens aperture. The beam is thus made to deflect over the specimen in the form of a raster. The raster action is similar to that which takes place in a television tube where electron beam sweeps out the screen area in 625 lines. Another useful facility desirable in certain applications is that of beam "chopping" i.e. the ability to turn the beam on and off if inserted near the filament of the microscope.

Many of the physical effects that occur when the probe strikes the specimen surface at a given point give rise to signals, which can be collected and amplified to give information about that that point. Each signal can be collected simultaneously and passed to the control grids of different display oscilloscopes, which are scanned synchronously with the electron beam in the main column. In this way, the same square raster is built up in the face of an oscilloscope and the brightness variations seen are due to signal variations from point to point on the specimen surface. For the sake of simplicity, only one amplifier is shown in

Figure (2.7). Every instrument has at least two oscilloscopes; one for video display with a long persistence time, the other for photographic recording.

For most practical purposes, the standard operating mode is the emissive mode in which mainly secondary electrons are controlled. The magnification of the microscope is controlled by the scan generator which varies the ratio of the raster size on the specimen to that on the video oscilloscope, the latter normally being100mm x 100mm. If the generator supplies voltage to make the specimen raster100μm x10μm, the effective linear magnification is 10^4. Obviously, as the magnification is increased, the angle of scan, which the beam makes over the specimen, is progressively diminished. On standard machines, a magnification range of perhaps20-50000X is available. To obtain the lowest magnification, the specimen must be lowered, thereby increasing the working distance and making spherical aberration more severe. Besides vertical movement, the stub, on which the specimen is mounted, can be rotated or tilted with respect to the incident beam, a procedure that increases the signal. If the specimen is tilted, foreshortening may occurand this should be allowed for when estimating magnifications (Fathers *et al.*, 1973).

The relationship that exists between the useful magnification and the probe size at the specimen may be seen as follows. Assume that the resolution of the eye is 0.1mm and the viewing raster has size b mm x b mm (b is usually 100) the number of raster lines which may be usefully displayed on the screen of oscilloscope is $\frac{b}{0.1}$. If the corresponding raster size on the specimen is s, the linear magnification M= $\frac{b}{s}$. The interval between the line scans on the specimen is given by x=$\frac{0.1s}{b} = \frac{0.1}{M}$, i.e. x is a factor of M. Clearly, the probe size d_f,

should be equal to x because if not, either the lines overlap ($d_f < x$). For M=100X, the focused spot size should 100nm, and for M= 10,000X, it is 10nm. The value of $d_f$is a strong function of the lens excitations, which should be adjusted correctly. Failure to fulfill the condition $d_f = x$ may give rise to misleading information. The simple treatment outlined here, though instructive, assumes the probe to be uniformly bright. In fact the intensity falls at the edge so that a more realistic condition is for the scan lines to be somewhat closer together than d_f(Fathers *et al.,* 1973).

2.3.3 Energy Dispersive X-Ray Spectroscopy

The properties of X-rays can be utilized in specimen microanalysis and are therefore of some relevance to electron microscopy. X-ray emission occurs when an inner shell is excited by the primary electron beam to leave the atom entire or go into higher unoccupied level. The vacancy is subsequently filled by another electron which drops from a higher energy level and emits an X-ray photon of energy hv equal to the loss ΔE by the electron in falling between the two shells (Joseph *et al.,* 2003).

EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Boron) to 92 (Uranium) can be detected in principle, though not all instruments are equipped for 'light' elements (Z less than 10). Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration standards of known composition. (Russ, 1984).

In this technique, when a high voltage focused electron beam strikes a solid specimen, it causes emission, absorption and fluorescence in the X-ray spectra region. The X- rays emitted are the characteristic of the kind of atoms present in the sample. The analysis of the emitted X-rays can be done in two ways known as energy dispersive (ED) and wavelength dispersive (WD). In the WD method, a crystal spectrometer is used to disperse emerging X-rays which impinges on the crystal in such a way that only photons of selected wavelength (those fulfilling the Bragg's law) reach the counter. The counter emits the voltage pulse whose height is proportional to the energy of each X-ray photon exciting it. Good resolution (about 1eV) for distinguishing between neighboring spectral peaks is achievable with WD system and it can cope with high generation rate X-rays. However, the geometrical arrangement of the component is critical. I the commonest form of the ED system, a lithium drifted silicon detector is sighted close to the sample and receives from it the whole wavelength spectrum of X-rays. The detector discriminates between various energy (and hence wavelengths) falling on it and the results are fed to a multichannel analyzer which displays the number of quanta corresponding to any particular X-ray. The ED system can accept simultaneously, wavelengths from any elements, is rapid and requires comparatively low probe current (< 1nA). The resolution of a solid state detector is about 150eV and (unlike the WD method) cannot be used for X-rays with energies less than 1keV.

2.4 PROCESSING OF ACTIVATED CARBON

Activated carbon can be produced by either steam or chemical activation, both of which require the use of elevated temperature.

Chemical activation is achieved by degradation or dehydration of the, usually cellulosic, raw material structure. Steam activation, however, initially involves the removal of volatiles, followed by oxidation of the structure's carbon atoms

2.4.1 Chemical Activation

The raw materials used in chemical activation are usually sawdust, coconut shell and most popular activating agent is phosphoric acid, although zinc chloride and sulfuric acid are well documented. Others used in the past include calcium hydroxide, calcium chloride, manganese chloride and sodium hydroxide, all of which are dehydrating agents can achieve the same objective. The raw material and reagent are mixed into a paste, dried and carbonized in a microwave . When phosphoric acid is the activating agent, the carbonized product is further heated at 400-500W, during which stage the carbon is oxidized by the acid. The acid is largely recovered after the activation stage and converted back to the correct strength for reuse (Liqiang *et. al*., 2013).

The activated product is washed with water and dried.

2.4.2Steam Activation

The use of steam for activation can be applied to virtually all raw materials. A variety of methods have been developed but all of these share the same basic principle of initial carbonization at 500-600 degrees C followed by activation with steam at 800-1,100 degrees

C. Since the overall reaction (converting carbon to carbon dioxide) is exothermic it is possible to utilize this energy and have a self-sustaining process.

A number of different types of kilns and furnaces can be used for carbonization/activation and include rotary (fired directly or indirectly), vertical multi-hearth furnaces, fluidized bed reactors and vertical single throat retorts. Each manufacturer has their own preference. (Manocha, 2003).

2.5 THEORY OF MICROWAVES

2.5.1 Microwave heating process

In order to overcome the apparent limitations of conventional heating methods, alternative heating methods have been developed and applied in science and technology. In this category, electro-heat technologies have emerged to include induction, radio-frequency, infrared and microwave heating, all utilizing specific parts of the electro-magnetic wave spectrum (Appleton *et al.*, 2005).

Microwave heating is a potentially attractive method as it allows for improved heating efficiencies compared to conventional methods. Magnetrons (microwave sources) were invented in 1940, initially for military purposes. After the war, microwaves were increasingly used in other applications. The first commercial microwave oven was developed and manufactured in early 1950. However, they were not used in industry until 1962. Since then, microwave heating has been successfully used in various industrial and domestic applications such as food industry, vacuum drying, pasteurisation and sterilization, ceramic, rubber and plastic industries, crude oil exploration and processing, forestry and

agriculture, as well as many other applications in chemical industry and civil engineering (Meredith, 1972).

The mechanism of microwave heating is different from conventional heating in terms of its "volumetric heating" effects and the "selective heating" which results in a more efficient heating of material. Unlike conventional heating methods, where material is heated through heat flux, microwave heating is achieved throughout the volume of material by direct conversion of electro-magnetic wave energy to heat as waves penetrate the substance (volumetric heating). As a result, the rate of heating is not limited by the thermal diffusivity of material and therefore more uniform heating is assumed to be achieved (Meredith, 1972). Also, microwave heating is referred to as selective heating, as electromagnetic wave energy is only dissipated as heat in materials with suitable dielectric properties and not necessarily everything in contact with them.

Although microwave heating is considered to be a beneficial alternative for conventional heating techniques in waste management and conversion processes, it is also worth mentioning that there are some limitations concerning microwave heating processes. These include; the absence of sufficient knowledge on the dielectric properties of materials such as biomass and the need of more complicated design and implementation of the technology, as well as uncertainty about the actual cost of these technologies (Fernandez and Menendez., 2011).

2.5.2 Microwave Heating Efficiency

Microwave heating efficiency could be named as one of the most important features of this method in comparison with the conventional heating techniques (Moseley *et. al.*, 2007).

Nevertheless, it should be noted that microwave heating efficiency depends on the type of application and material being heated. As stated earlier, the type of material being heated has a profound influence on the efficiency of microwave heating process; in other words, according to their microwave responsivity some materials cannot be efficiently heated by microwaves. In general, it can be concluded that the benefit of using microwave heating can be substantial only when applied to suitable material; this is of more significance when heating time is a crucial factor, as the slow heating rates achievable by conventional methods results in considerably high energy consumption (Moseley *et. al.*, 2007)..

2.5.3 Microwave Heating Mechanism

Microwaves are of frequencies between radio waves and infrared radiation (300 MHz to 300 GHz), corresponding to wavelength of 1mm to 1m, which are mainly used for communicational purposes. Frequencies close to 900 MHz (896 MHz in the UK) with wavelength of 33.3 cm and 85% efficiency and 2450 MHz with wavelength of 12.2 cm and 80% efficiency have been designated to be used in industry. All domestic microwave ovens operate at 2450 MHz. These frequencies, often named ISM (Industrial, Scientific and Medical) frequencies, have been selected with the aim of minimum interference with communicational services (Meredith, 1998).

The interaction between microwaves and material can be in from of absorption, reflection and transmission, according to which materials are categorized into absorbers, conductors and insulators, respectively (Fernandez *et al.*, 2011). The main interactions are absorption and reflection. In fact, energy in the form of heat through microwaving is initially generated

via absorption; transmission is in fact the result of incomplete absorption and partial reflection (Clark *et.al.,* 2014).

Microwave radiation, like all other EMR, consists of oscillating electric and magnetic fields. If microwave electric field is passed over a water molecule, the positive and negative areas of the molecule will interact with the positive and negative areas of the moving field. This forces the water molecules to oscillate resulting in friction between the molecules. This friction then leads to heating. Materials that absorb microwave radiation are called dielectrics, thus, microwave heating is also referred to as dielectric heating.

The understanding of principles of microwave heating requires the definition of specific terms, most important of all are "*dielectrics"* and "*dipoles".* An electric dipole consists of two equal and opposite charges, located at a certain distance. Many molecules intrinsically carry dipoles due to their non-uniform distribution of positive and negative charges on various atoms.

Accordingly, a molecule with permanent dipoles is termed polar molecule. Dielectric materials are electrical insulators (or partly insulators) which do not contain dipoles intrinsically, however can be polarized when placed in an electrical field. Dielectric polarization occurs through minute changes in the charges of the molecules in insulating or partly insulating materials. Dielectric materials are different from conductors because charges in dielectrics are held by atomic or molecular forces and are not able to move en-masse as occurs in conductors when passing an electric current (Clark *et.al.,* 2014).

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Regardless of the origin of dipoles, dipolar components tend to physically align with the electric field once introduced to an electromagnetic field. (Thostenson and Chou, 1999,

Meredith, 1998,). The extent of which microwaves interact with materials depends on the materials' dielectric characteristics including permittivity, electrical properties and permeability, as discussed below.

2.5.4 Permittivity and Permeability

Microwaves, as with all electromagnetic waves, consist of an electric (*x* component) and a magnetic (*y* component) field, oscillating perpendicular to each other as shown in Figure 2.9. The fields can be expressed as:

$$\underset{E}{\rightarrow} = \mathrm{E}_0 e^{-\gamma z}\mathrm{x} \qquad (2.11)$$

$$\underset{H}{\rightarrow} = \frac{\mathrm{E0}}{\sqrt{\mu/\varepsilon}} e^{-\gamma z}\mathrm{y} \qquad (2.12)$$

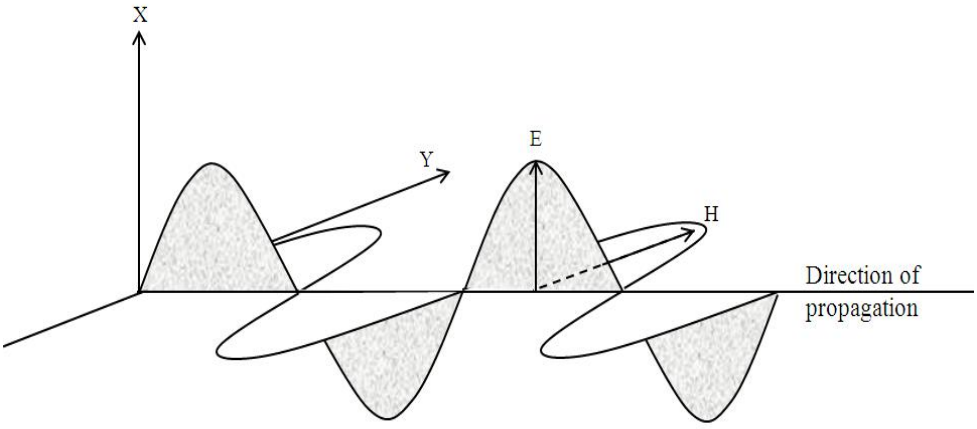


Figure 2.8 Travelling electromagnetic wave through a loss-free dielectric,

adopted from Von Hippel, 1954

Where E_0 is the amplitude of the electric field, γ is the propagation constant, ε the material's permittivity and μ is the permeability. Permeability is the ability of material to support the formation of magnetic field within itself. However, the effect of permeability in non-magnetic materials is negligible, thus it plays a less significant role in the heat conversion throughout microwave heating. Therefore, the capability of materials in absorbing the microwaves and heat conversion is more governed by their dielectric properties in terms of their real dielectric constant or permittivity, relative dielectric constantε', effective loss factor $\varepsilon''_{\text{eff}}$ and loss angle δ. The relative dielectric constant or permittivityε', is the permittivity of material relative to that of free space and represents the ability of a dielectric to store the potential electric energy if placed in an electric filed. The effective dielectric loss factor, $\varepsilon''_{\text{eff}}$, is representative of the efficiency of conversion of absorbed energy to heat (Lidström et al., 2001, Von Hippel, 1954). To account for all losses, the dielectric content for a real dielectric is expressed in terms of the complex permittivity,

$$\varepsilon^* = \varepsilon' - j\varepsilon''_{\text{eff}} \qquad (2.13)$$

An important parameter in characterisation of dielectric materials is their loss angle, which is expressed as the ratio of real permittivity and the loss factor, seen in Equation 2.13

$$\tan\delta = \frac{\varepsilon''\text{eff}}{\varepsilon'} \qquad (2.14)$$

When a dipole is placed in an electric field, it will try to reorient to the variations of the alternating voltage of the field. The re-orientation of dipoles and charge displacement results in an electric current known as Maxwell displacement current. The parameter δ in Equation

2.14 represents the phase displacement caused by the dipole lag behind the electric field, i.e. the lag between the re-orientation of dipoles with the electric field oscillation.

Along with the heat capacity and density of the material, the dielectric loss is helpful in enabling comparison between materials in terms of their heating rates under the influence of an electromagnetic field. The permittivity of dielectrics is usually measured at either a single frequency, or frequency spectrum, as a function of thermodynamic parameters such as temperature, pressure and sample composition (Christof, 2010).

2.5.5 The Suitability of Materials for Microwave Heating

The microwave heating of materials is most probably restricted by their dielectric properties. As discussed earlier, not all materials can be heated by microwaves this being dependent upon the ability of molecules to couple with the microwaves, i.e. their dielectric properties. Two quantitative terms indicative of the suitability of materials to be microwave processed are power absorbed per unit volume (*PA*) and depth of penetration (*Dp*), where the former is expressed as:

$$P_A = 2\pi f \varepsilon''_{\text{eff}} \varepsilon_0 E_{\text{rms}}^2 \qquad (2.15)$$

In which f is the frequency (Hz), ε_0 is the permittivity of free space and the E_{rms} is the root mean square of electric field strength in material (V/m). (Thostenson and Chou, 1999).

It should be noted that this equation is only valid for very thin materials where the electric filed can be considered to be constant. This is because the electric field loses its influent at further distances from the surface. Accordingly, the penetration depth (D_p) is defined as

distance from the surface of sample where the absorbed power is at a specific ratio (*1/e*) of the power at the surface of the material. A simplified form of microwave penetration depth is given by the following equation (Thostenson and Chou, 1999):

$$D_p = \frac{c}{2\pi f \varepsilon'' \text{eff}} \quad (2.16)$$

Where*C* is the speed of light in vacuum. This parameter is particularly important in processing of thick materials. If the penetration depth of microwaves is much less than the material thickness, the rest of the material is heated by conduction.

2.5.6 Microwave structure and parts

The structure of the microwave oven, as well as its output power, has a significant effect on the heating of objects. This implies that changes in the configuration of a system such as single or multimode microwaves ovens, shape and size of the cavity, shape and type of the reactor and its position within the microwave cavity, could induce considerable changes in the heating behaviour of the material under test. Although this characteristic of microwave heating can make the process receptive to uncontrollable changes, it also provides an element of versatility to the production method through making simple adjustments to the above factors. Therefore, understanding the mechanism through which electromagnetic waves are produced and delivered to the material in a microwave heating system is indispensable. The mechanical structure of a microwave oven generally consists of a high voltage power supply, microwave source, transmission lines, cooling system and applicator.

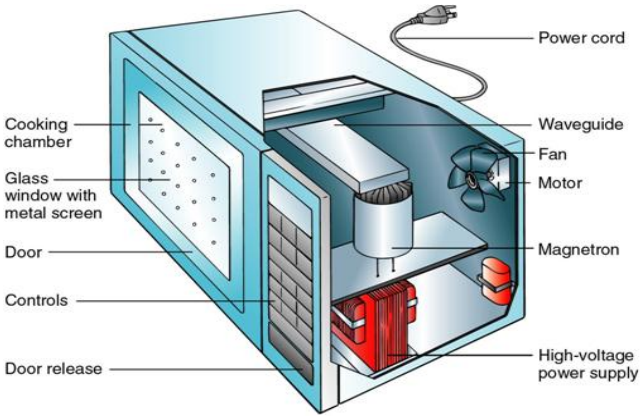


Figure 2.9 Schematic diagram of mechanical structure of a typical microwave oven (Modified from Vollmer, 2011).

The power system is responsible for producing the high voltage current which later is converted to electromagnetic waves through charge acceleration in the microwave source.

2.5.7 Microwave Sources and transmission lines

The most common microwave sources are Magnetrons and Klystrons. Generally, Magnetrons are favourable due to their frequency stability, higher efficiency and lower cost due to mass production. On the other hand, Klystrons are capable of producing higher powers and benefit from longer life time (up to eight times higher than magnetrons), although they tend to be more expensive (Bradshaw et al., 1998, Thostenson and Chou, 1999).

Magnetrons produce microwaves ranging from 1 to 40 GHz at ~80% efficiency and 5,000 hrs lifetime. The internal structure of magnetron comprises of a cylindrical cathode placed on the axis of a circular anode, in a vacuum tube. The anode contains cavities which are

designed to act as a resonator for operating microwave at high frequencies. A permanent magnet or an electromagnet is placed around the anode which produces a high density magnetic field (Vollmer, 2011).

The transmission lines (wave guides) can be made in several shapes (rectangles, circular tubes or elliptical forms) from conductive materials such as copper, brass, silver and aluminium or other similar materials with low bulk resistivity. Other components could be also located in the transmission lines system to protect the equipment, for sensing purposes and coupling microwaves with materials in the applicator (Thostenson and Chou, 1999).

2.5.8 Applicator

The microwave applicator refers to the space where microwave energy is coupled with the subject material. Microwave coupling with material is strongly influenced by the applicator size and geometry, material size and location and the size and shape of the material relative to the applicator, as well as the subject material's dielectric properties.The domestic microwave ovens to be used in laboratories are usually modified for a specific application. (Bradshaw *et al.*, 1998).

2.5.9 Role of microwave heating

When microwave heating is applied to a heating process, the heating rate and the residence time of volatiles are observed when compared with those achieved by conventional heating. Conventional heating means that heat is transferred from the surface towards the center of the material by convection, conduction and radiation. On the contrary, microwave heating represents the conversion of electromagnetic energy to thermal energy via dipole rotation

and ionic conduction. Because microwaves can penetrate materials and deposit energy, heat can be generated throughout the volume of the material, rather than from an external source (volumetric heating). Therefore, microwave heating is energy conversion rather than heat transfer. In microwave heating the material is at higher temperature than the surrounding area, unlike conventional heating where it is necessary that the conventional furnace cavity reach the operating temperature, to begin heating the material. Consequently, microwave heating favours the reactions involving the solid material, e.g. devolatilization or heterogeneous reactions (Zhang & Hayward, 2001).

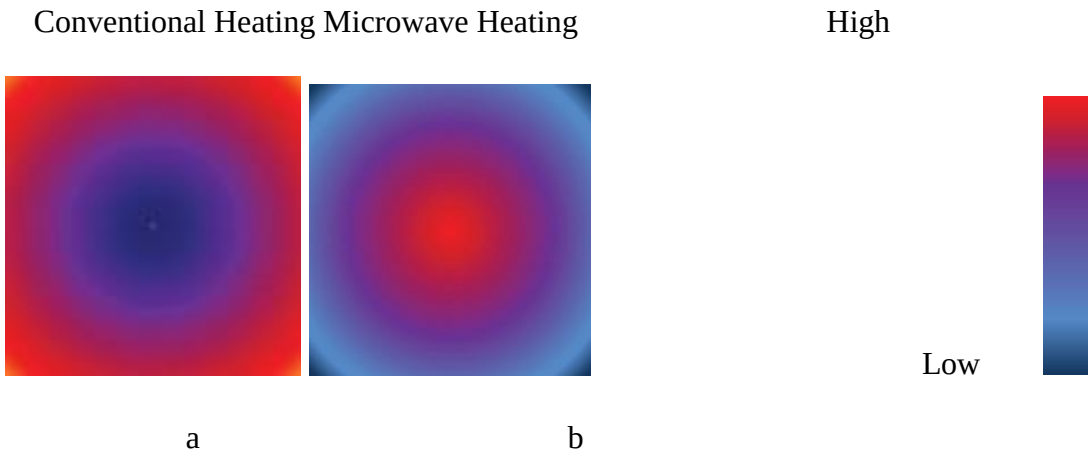


Figure2.10 Quality comparison of temperature gradient within samples heated by (a) conventional heating and (b) microwave dielectric heating. While the circles represent the sample, the squares correspond to the cavity used in both heating systems (Fernández, 2010)

From the different thermal gradients, it can be assumed that there are differences in final yields and composition of the heated products under both heating systems (Menéndez *et al.*, 2004; Domínguez *et al.*, 2007). The differing performance between conventional and

microwave heating is also translated into differential heating rates of the material. Microwave heating reveals higher heating rates due to the fact that microwave energy is delivered directly into the material through molecular interaction with the electromagnetic field, and no time is wasted in heating the surrounding area. Therefore, significant savings of time and energy are achieved in MP, although other effects can also be deduced affecting the volatiles profiles. (Minkova *et al.*, 2001).

2.6 FACTORS AFFECTING MICROWAVE ASSISTED ACTIVATED CARBON PRODUCTION

(a) Raw material

The nature of raw material determines how much of the microwave energy that would be absorbed. Most organic materials rich in carbon can be used as raw material for the manufacture of AC (Rodriguez-Reinoso, 1991). In the selection of raw materials for preparation of porous carbon, several factors are taken into consideration. The factors are:

i. High carbon content

ii. Low inorganic content (i.e low ash)

iii. High density and sufficient volatile content

iv. Stability of supply in the countries

v. Potential extent of activation

vi. Inexpensive material

vii. Low degradation upon storage

Low content of inorganic materials is important to produce AC with low ash content, but relatively high volatile content is also needed for the control of the manufacturing process.

Raw materials such as coconut shell are very popular for many types of AC, because their relatively high density, hardness and volatile content are ideal for manufacture of hard granular AC. (Manocha*et. al.,* 2003).

(b) Microwave Power: An increase in microwave power increases the temperature of the activated carbon and thus, the increase in activity. The larger the input microwave power, the more rapidly the temperature of activated carbon bed rises and the higher the temperature reaches in quasi-stationary stage. (Bathen, 2003; Liu *et. al.,* 2010;Alireza et al., 2010; Liqiang Zhang*et. al.*,,2013).

(c) Temperature: Temperature, particularly the final activation temperature, affects the characteristic of the activated carbon produced. Generally, for commercial activated carbon usually conducted at temperature above 800°C in a mixture of steam and CO_2. Recently, researchers have been working out on optimizing the final activation temperature to economize the cost of production and time (San Miguel, *et al.,* 2003).

(d) Activation time: Besides activation temperature, the activation time also affects the carbonization process and properties of activated carbon. From previous study, the activation times normally used were from 10 minutes to 30 minutes for coal and coconut shell. As the time increased, the percentage of yield decreased gradually and the BET surface area also increased. This result is possibly due to the volatilization of organic materials from raw material, which results in formation of activated carbon(Liqiang Zhang *et. al.,* 2013).

CHAPTER THREE

MATERIALS AND METHOD

3.1 MATERIALS

Thefollowing are a list of materials/equipments that were used for the research:

i. Beakers (100ml)
ii. Measuring Cylinders
iii. Hot plate (C- MAGHS10)
iv. Microwave oven (SINGSUNG 19L4)
v. Palm kernel Shell
vi. Coconut Shell
vii. Sodium Chloride
viii. Calcium Chloride
ix. Glycine
x. Ethylene Glycol
xi. Oven (CHENSANG JIN-BOMB)
xii. Crucible and pestle
xiii. Methylene blue
xiv. Volumetric flask (1000ml)
xv. Filter papers
xvi. SEM coupled with EDS (Phenom Pro X)
xvii. XRD(PANalytical BV, Netherlands)
xviii. Spectrophotometer (Jenway 6405)

3.2 METHODOLOGY

Production of activated carbon was carried out employing Microwave-assisted chemical activation method. In this method, palm kernel shell and the coconut shell was dried for 24 hours, ground and crushed to granular sizethrough a mesh of 125μm to remove unwanted particles.Five samples of the mixture of palm kernel and coconut shell were prepared containing 5g each of palm kernel and coconut shells.The mixture was done in the ratio 1:1.The chemical activation was achieved via a two-stage microwave heating involving partial thermal decomposition of the raw materials in 0.1M solution containing varying concentration of sodium chloride and glycine (amino acetic acid) and subsequent activation of the derivatives in 0.1M solution containing varying concentration of calcium chloride and ethylene glycol. The complete activation process for all the samples was achievedin 20 minutes with maximum power via microwave oven with power level ranging from 700W and maximum frequency of 50Hz.The proportion of Sodium Chloride and Calcium Chloride mixture for the 5 Samples of activated carbon at an activation time of 20 minutes was carried out as indicated in table 3.1.

Table 3.1 Proportion of Sodium Chloride and Calcium Chloride mixture for the 5 Samples

Sample	Volume of Calcium Chloride (ml) at 0.1M	Volume of Sodium Chloride (ml) at 0.1M
Sample A	50	50
Sample B	60	40
Sample C	70	30
Sample D	80	20
Sample E	90	10

The activation process was done in twenty (20) minutes via microwave oven (SINGSUNG MODEL NO; 19L 4.DIMENSION; 262mm (H)X 452mm (W) X 337mm (D)) in which 700W power was used and a microwave irradiation heating frequency of 2.45GHz. After activation, the activated carbon produced was washed with distilled water several times until the residual activating agent on the surface of activated carbon was completely removed. This stage is done because during impregnation, the activating agent will penetrate into raw material particles and occupy substantial volumes. Once they are extracted by intense washing, a large amount of micro porosity will be created. The characterization of the activated carbon was done using XRD, SEM coupled with EDS. The structure of the produced activated carbons was elucidated using an XPERT-PRO Diffractometer (PANalytical BV, Netherlands) which was equipped with Cu-K_α radiation operating at 40 kV and 30 mA. The goniometer is equipped with an automatic divergence slit and PW3064 spinner stage. The XRD pattern of the produced activated carbon samples were recorded in the range $10^o < 2\theta < 90^o$ with a step size of 0.02^o and step time of 2.5 second. As a follow-up to the XRD analysis, the morphology and elemental composition of the produced activated carbons were investigated using Scanning Electron microscope (Phenom Pro X), which was equipped with tungsten source and coupled with an Energy Dispersive X-ray spectroscope. The effectiveness of the activated carbon for removal organic dyes from water contaminated with organic dyes was tested via adsorption studies using the Freundlich and Langmuir model.

3.3PRELIMINARY STUDIES

3.3.1 Estimation of Moisture Content

1.0g of the dried activated carbons were weighed and placed in washed, dried and weighed crucible. The crucibles and samples were placed in a microwave and dried to constant weight for 20 minutes according to the method of Rengaraj*et. al.,(2002)*. The percentage moisture content (%MC) was computed as follows:

Mass of crucibles +original Sample = (b)g
Mass of crucible + sample after drying = (c)g
Moisture content = (b – c)g

$$\% \text{ moisture content} = \frac{(b-c)g \times 100}{2.0g} \quad (3.1)$$

3.3.2 Estimation of Ash content

A clean crucible was kept in the microwave and heated at full power for 20minutes. This was cooled and weighed at room temperature. 10g of each of the activated carbonsample was weighed into the crucible. The crucibles along side with the activated carbon samples were placed in the microwave and heated for another 30 minutes. This was done to obtain ashing.The ashed samples were then cooled and weighed at room temperature . The percentage of the ash content was calculated as shown below;

$$\%\text{Ash} = \frac{\text{W3}-\text{W1}}{W2-W1} \times 100 \quad (3.2)$$

where
W1 = mass of empty crucible (g)

W2= mass of crucible + dried sample (g)

W3= mass of crucible + ashed sample (g) (Rengaraj*et. al.*, 2002)

3.4 Test on Adsorption of Dye (methylene blue)

1g each of the samples was used for this test. 10, 20, 30, and 40mg/L of the dye (methylene blue) was prepared. The activated carbon was added into 50ml of MB solution and then transferred into labeled sample bottles. The respective samples were introduced into the dye (Methylene Blue) solutions and shaken thoroughly using a mechanical shaker for 30 minutes to attain equilibrium condition for adsorption to be established. Thereafter the different activated carbons were filtered and the absorbance was measured. The concentrations of MB before and after adsorption were determined using a Jenway 6405 UV/Spectrophotometer at 668 nm wavelength. The amount of adsorption at equilibrium, q_e (mg/g) was calculated by the formula:

$$q_e=(C_o-C_e)V/m \quad (3.3)$$

where,

C_0 = liquid-phase concentration of the dye at initial concentration (mg/L)

C_e= concentration of the dye at equilibrium state

V = volume of the solution (L) and

m = mass of dry adsorbent used (g).(Malik, 2004).

3.4.1 Adsorption Isotherms

Equilibrium behavior of adsorbents usually determine the adsorption isotherm at which the functional equilibrium distribution of adsorption with concentration of adsorbate in solution

at constant temperature. The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and solid phase when the adsorption process reached equilibrium stage. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. Several equilibrium models have been developed to describe adsorption isotherm relationships. Two isotherm equations were tested in this work; they are Langmuir and Freundlich isotherm. The applicability of the isotherm models were evaluated by correlation coefficients, R^2 value of each plot. The higher the R^2 value, the better fit to the model.

3.4.1.1 Freundlich Isotherm

Freundlich model was used in determination of the isotherm given by the equation

$$q_e = K_f C_e^{(1/n)} \quad (3.4)$$

where

q_e = amount adsorbed at equilibrium (mg/g)

C_e = equilibrium concentration of the adsorbate (MB) (mg/L) and

K_f= adsorption capacity of the adsorbent (mg/g) (Malik, 2004).

n giving an indication of how favorable the adsorption process and 1/n indicates the adsorption intensity of the adsorbent. K_f can be defined as the adsorption or distribution coefficient and represents the quantity adsorbed onto activated carbon adsorbent for a unit equilibrium concentration. Normally, if the K_f value increase, the adsorption capacity will increase too.

Equation (3.4) can be linearised to give;

$$\text{Log}q_e = \log K_f + \frac{1}{n}\log C_e \quad (3.5)$$

The slope 1/*n* ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The value of n>1 represents favourable adsorption condition. The plot of log q_e versus log C_e gives straight lines with slope '1/*n*' and an intercept of log K_f, which shows that the adsorption of MB also follows the Freundlich isotherm (*Li et al., 2009*).

3.4.1.2 Langmuir Isotherm

Langmuir Isotherm equation has been widely applied to describe experimental adsorption data based on the assumption that adsorption energy is constant and independent of surface coverage; that adsorption occurs on localized sites with no interaction between adsorbate molecules, and the maximum adsorption occurs when the surface is covered by a monolayer adsorbate (Malik, 2004). The theoretical Langmuir Isotherm equation can be expressed as ;

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (3.6)$$

.

where

Q_0 = maximum amount adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage on the surface bond,

b = constant related to the affinity of binding sites

q_e=`amount adsorbed at equilibrium time (mg/g) and

C_e = equilibrium concentration of the adsorbate (mg/L).

The constant Q_0 is the maximum amount adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage on the surface bond, b is the constant related to the affinity of binding sites, q_e is the amount adsorbed at equilibrium (mg/g).

The constant Q_0 and b can be determined from the following linearised form of Eq (3.6)

$$\frac{C_e}{q_e}=\frac{1}{Q_0 b}+\frac{1}{Q_0}(C_e) \quad (3.7)$$

A plot of C_e/q_e versus C_e will obtain a straight line with a slope of 1/ Q_0 and an intercept of $\frac{1}{Q_0 b}$.(Malik, 2004)

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 INTRODUCTION

This chapter summarizes the analysis of the results obtained from the samples prepared for this study. This include adsorptive studies, characterization of the activated carbon derived from coconut shell and palm kernel shell using Scanning Electron Microscopy (SEM), Energy- Dispersive X-ray Spectroscopy (EDS) and X-ray Diffraction (XRD) discussion of the result found in the course of the research.

4.1 Preliminary studies

The table below shows information and values of the preliminary studies of the various samples.

Table 4.1: Moisture content and Ash content percentage of samples used.

S/N	Samples	Moisture Content (%)	Ash Content (%)
1	Sample A	7.21	3.93
2	Sample B	6.82	3.70
3	Sample C	7.00	4.01
4	Sample D	6.56	4.22
5	Sample E	6.50	3.66

The result in table 4.1 above gives information about the moisture content and ash content of the various samples of the activated carbon. The ash content is useful in assessing the quality, kind and utility of the mineral content. The moisture content in allthe samples fall within the acceptable range of less than 70%, according toTierney *et al*., 2006, which indicates that the adsorption of moisture by the samples is also less. Among the carbon,

sample E has the least moisture content of 6.50 %. A good activated carbon must have low ash content. A small increase in ash content causes a decrease in adsorptive properties of activated carbon. As activation time and microwave power increases, ash contents of the samples increase. Ash content can lead to increase hydrophilicity and can have catalytic effects, causing restructuring process during regeneration of used activated carbon.The results in the Table 4.1 indicatesthat moisture content and ash content in all the samples is less, which suggests that the samples used are viable for adsorption.

4.2ADSORPTIVE STUDIES

4.2.1 Adsorption Isotherms

In this section, two isotherm models (Freundlich and Langmuir) were used. An analysis of the isotherm data by fitting them to different isotherm models was done to find the suitable model that can be used.

The figures below give the adsorption isotherms using Freundlich model of the samples from Sample A to E.

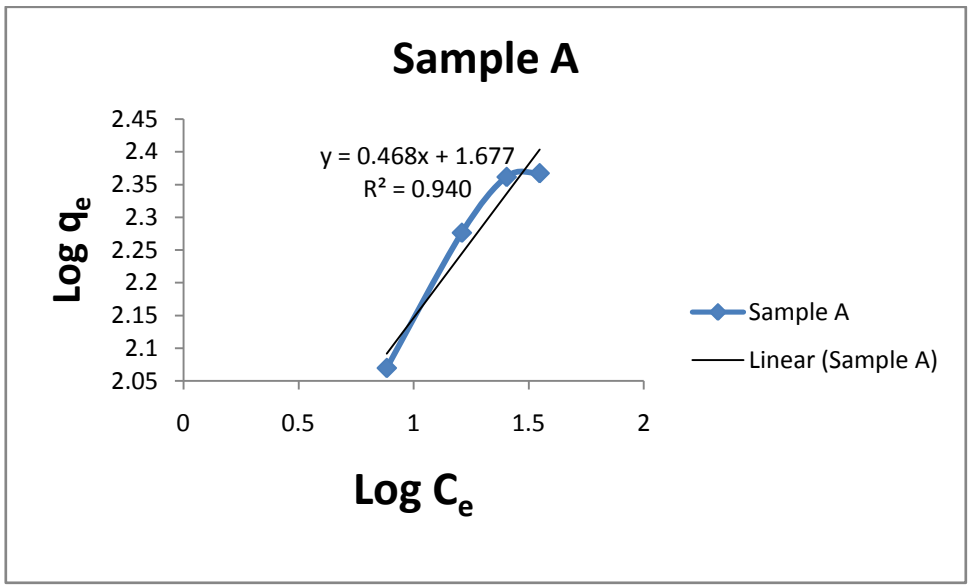


Figure 4.1: Sample A isotherm using Freundlich model

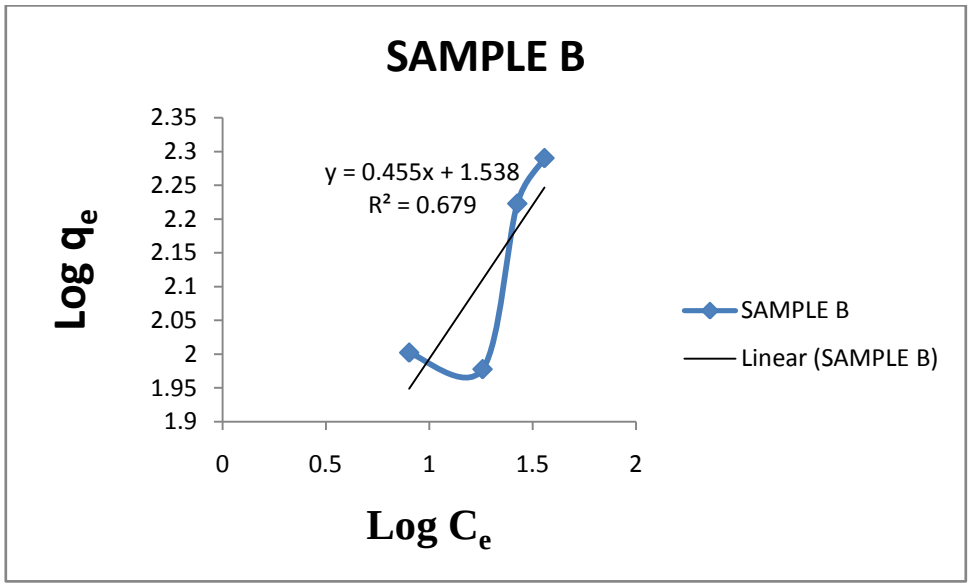


Figure 4.2: Sample B isotherm using Freundlich model

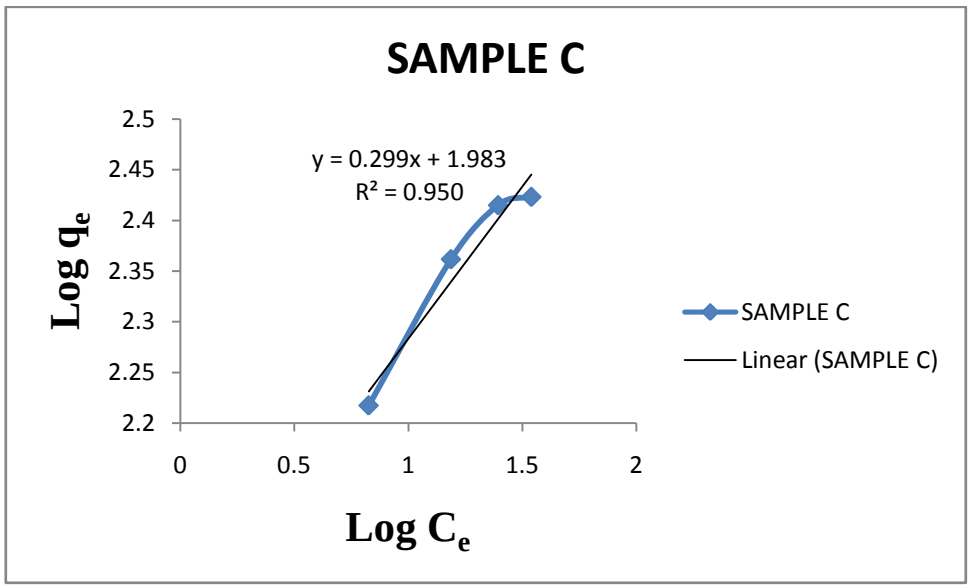


Figure 4.3: Sample C isotherm using Freundlich model

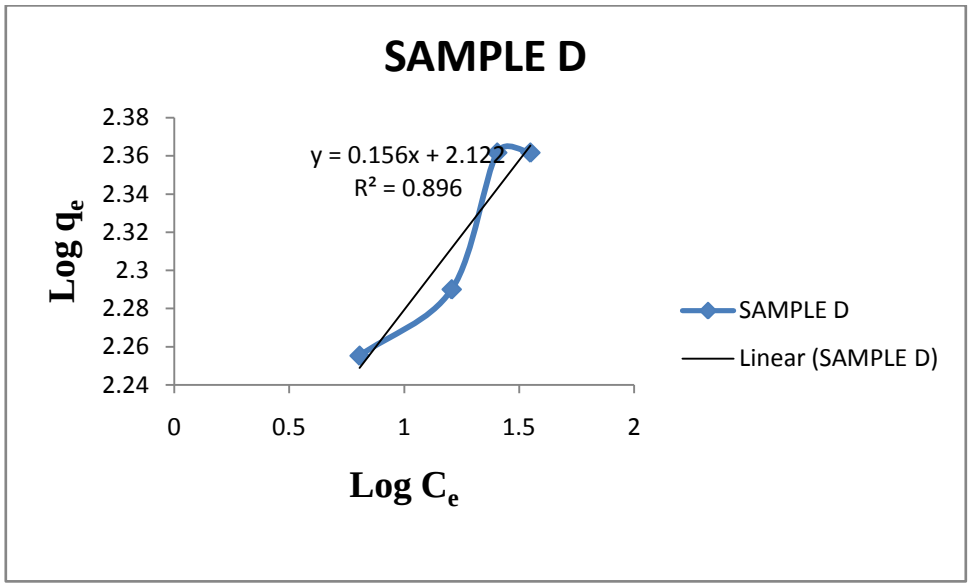


Figure 4.4: Sample D isotherm using Freundlich model

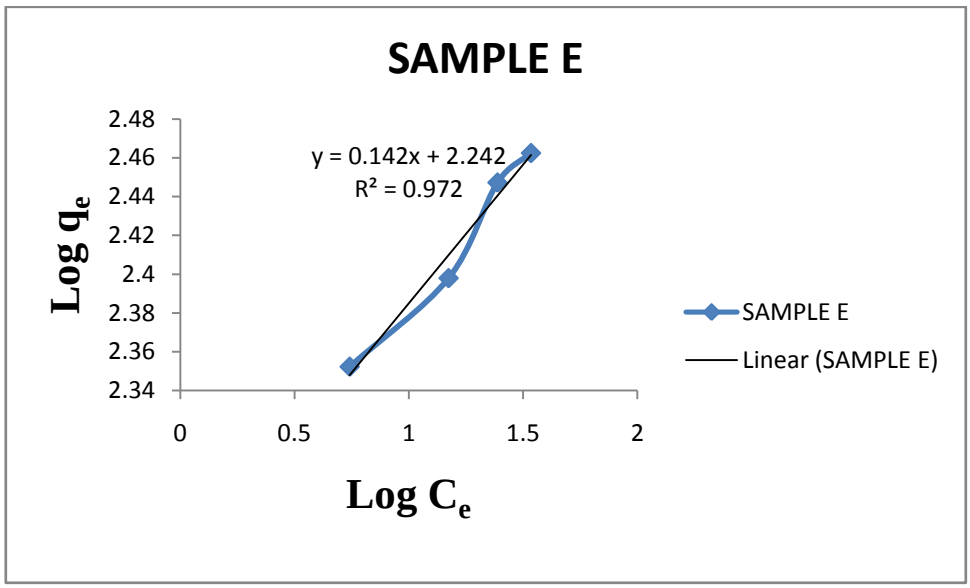


Figure 4.5: Sample E isotherm using Freundlich model

The figures below give the adsorption isotherms using Langmuir model of the samples from Sample A to E.

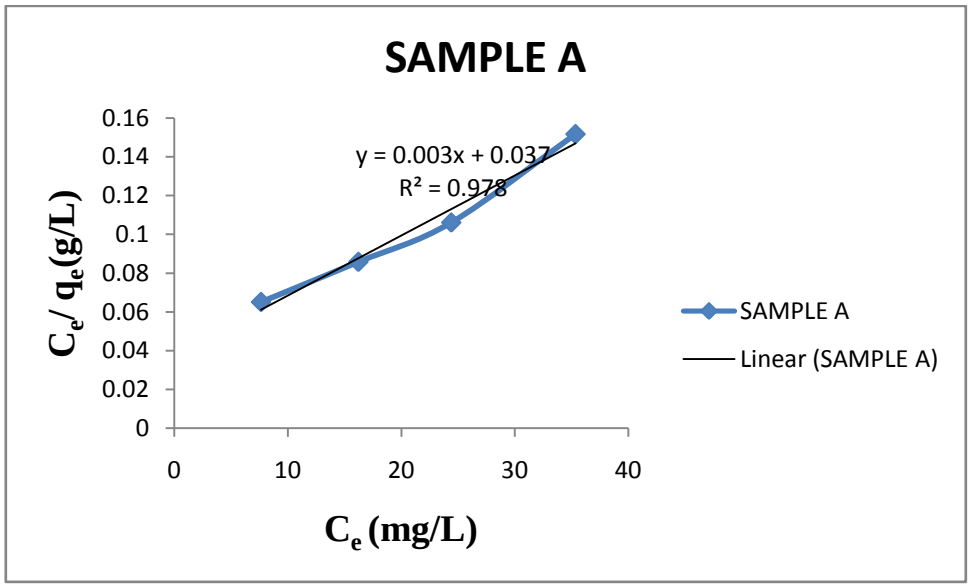


Figure 4.6: Sample A isotherm using Langmuir model.

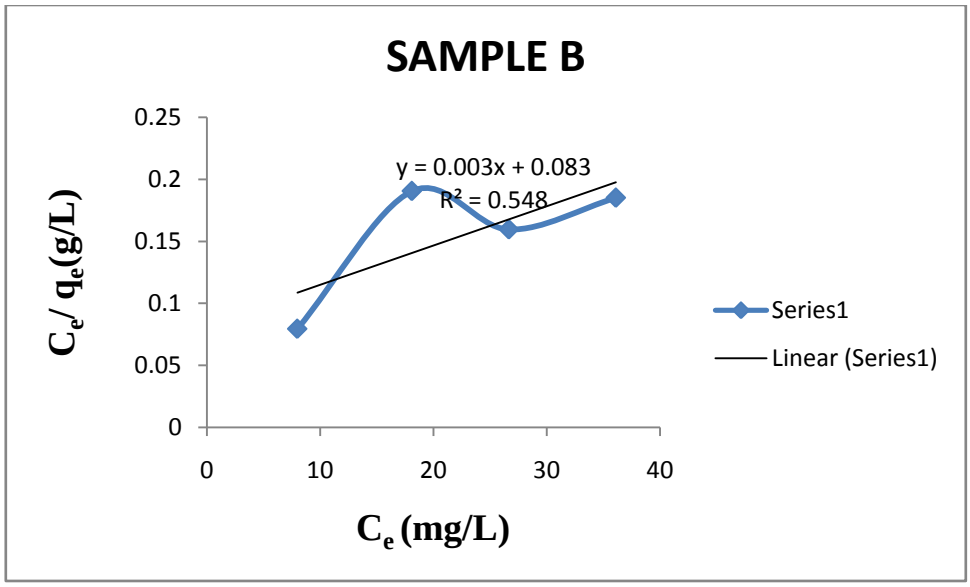


Figure 4.7: Sample B isotherm using Langmuir model.

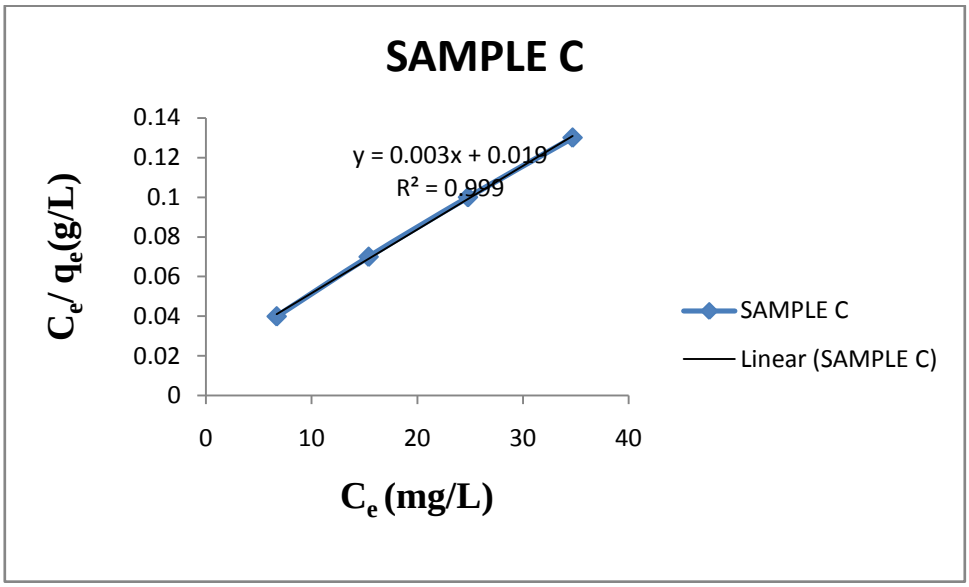


Figure 4.8: Sample C isotherm using Langmuir model.

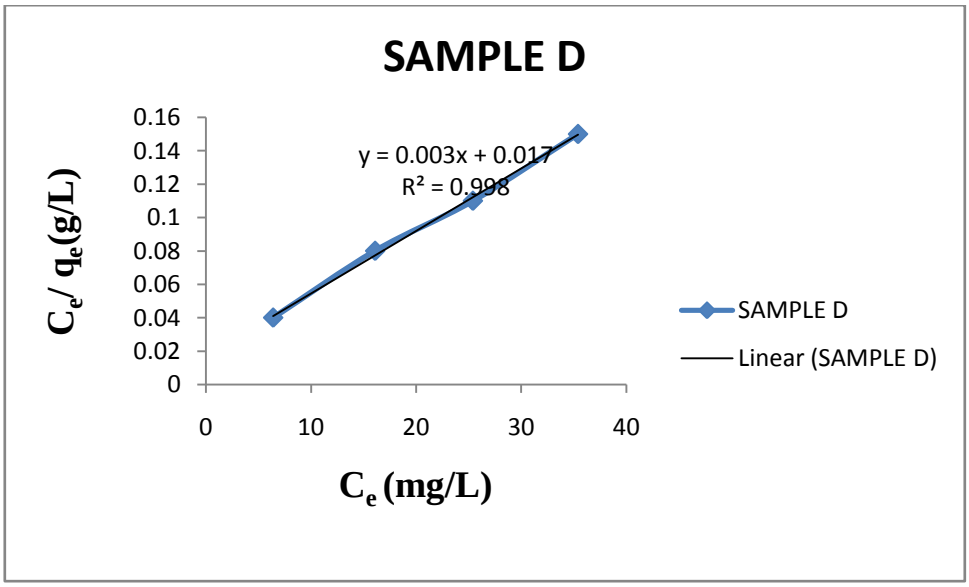


Figure 4.9: Sample D isotherm using Langmuir model.

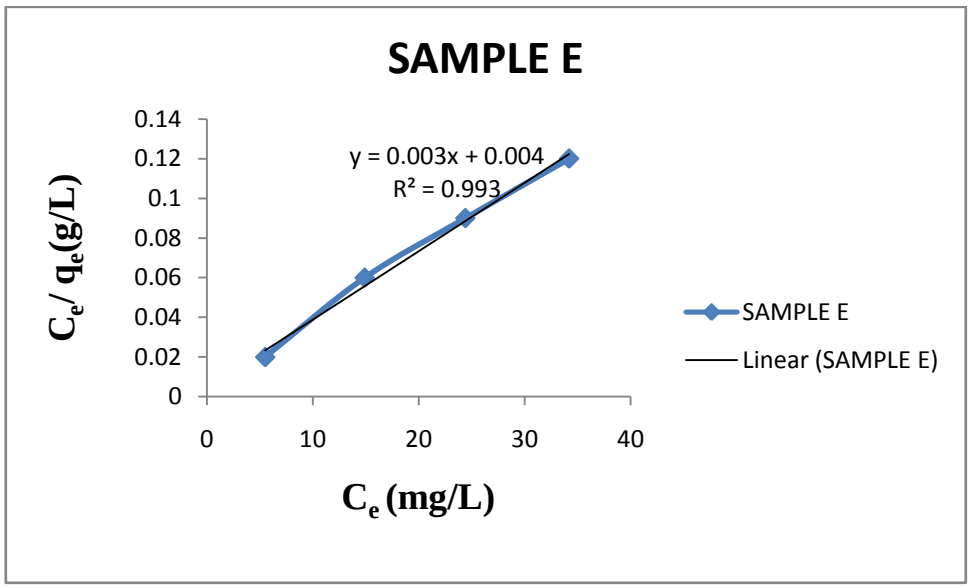


Figure 4.10: Sample E isotherm using Langmuir model.

The equilibrium adsorption data were interpreted using Langmuir and Freundlich models. The applicability of the isotherm equation was compared by judging the correlation coefficients, R^2. From figures 4.1- 4.10, the experimental data can be fitted well into the Langmuir isotherm model due to the fact that all the R^2 values lie in the acceptable range (R^2> 0.90) except sample B (R^2= 0.548). The result showed the formation of monolayer coverage of dye molecule at the outer surface of AC samples. Values of Q_o and b were obtained from the slope and interception of the linear plots, as presented in Table 4.13.

For Freundlich isotherm, the experimental data can be fitted well only for Sample A, C and E because their R^2 value was greater than 0.90 while Samples B and D had R^2 values lying below the acceptable range. Consequently, it indicated that Sample A, C and E also exhibits a multilayer adsorption phenomenon instead of monolayer coverage. However, for Samples B and D, the R^2 values were 0.68 and 0.89 respectively which showed poor agreement with Freundlich isotherm. On the other hand, the results suggest that MB dyes were favorably

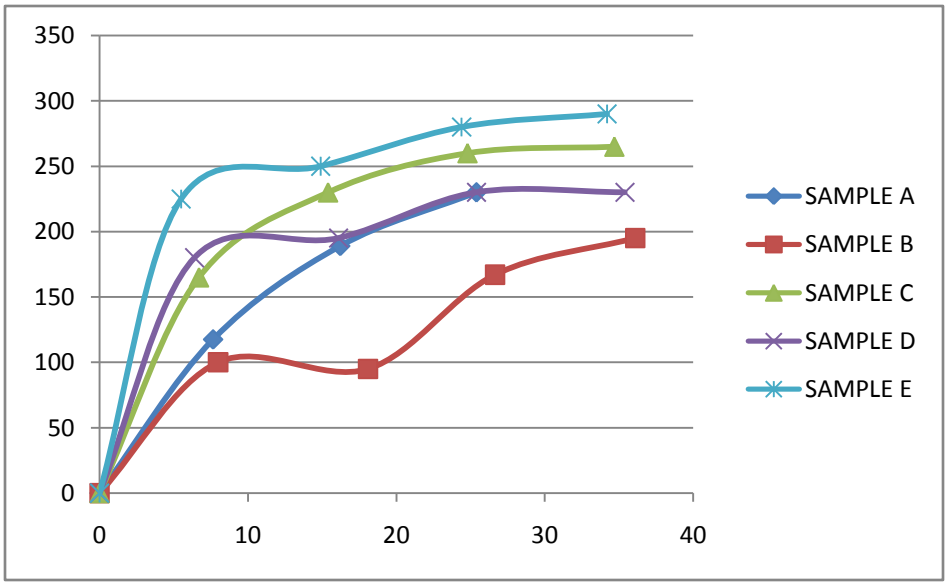
adsorbed by all prepared samples of activated carbon since the values of constant n were greater than the unity (n>1).

Based on the overall adsorption performance, the Langmuir isotherm was the best fit for the adsorption of MB on coconut shell and palm kernel shell activated carbon. This was because most of the correlation coefficient value (R^2) for Langmuir isotherm were more than 0.90, whereas for the Freundlich isotherm, some of the values fluctuated and were less than 0.90. The adsorption of Methylene Blue (MB) was best represented by Sample E which indicates that Sample E has the highest quantity of MB adsorbed onto the activated carbon adsorbent for a unit equilibrium concentration implying that it has a better microporous structure. Thus, more microporous structure of activated carbon would give rise to more adsorption capacity.

4.2.2Adsorbent Comparison

The figure below showsa comparison of the activated carbon samples on the adsorption of Methylene Blue which was obtained from the data below where q_e is the amount adsorbed at equilibrium time (mg/g) and C_e is the equilibrium concentration of the adsorbate (mg/L).

q_e (mg/g)



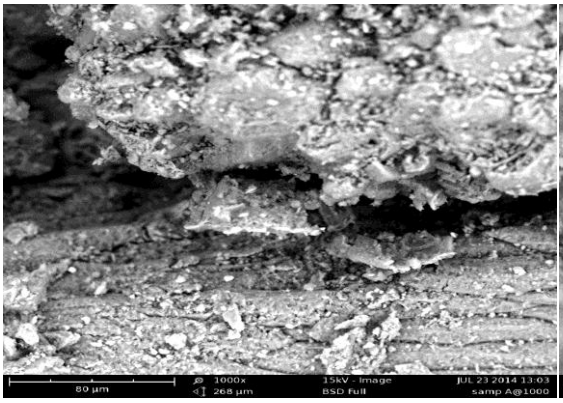
C_e (mg/l)

Fig 4.11 Comparison of activated carbon samples on the adsorption of Methylene Blue.

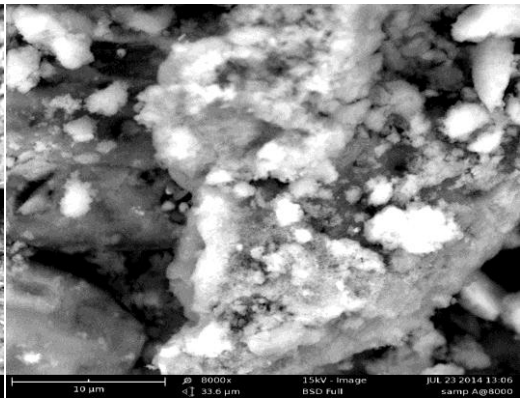
Figure 4.11 compares the adsorption capacities of the five adsorbents of MB prepared at the optimal conditions of microwave radiation power of 700 W, microwave radiation time of 20 minutes and impregnation time of 30 minutes. The figure shows the shape and varying adsorption amount for MB.The activated carbons samples have adsorption capacity increasing from 95mg.g^{-1} to 290mg.g^{-1}. The result indicated that sample E has the highest adsorption capacity of 290mg.g^{-1}. Chafia Bouchelta *et al.*, (2012) prepared coal based AC by microwave assisted chemical activation, where they achieved a maximum MB adsorption of 122.94mg.g^{-1}. The maximum adsorption of 277.8mg.g^{-1} was obtained by Roozbeh *et al.*, (2013) where they used apple pulp and apple peel to prepare activated carbon by using microwave method with phosphoric acid chemical activation.

4.3 SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS OF MICROWAVE ASSISTED ACTICATED CARBON

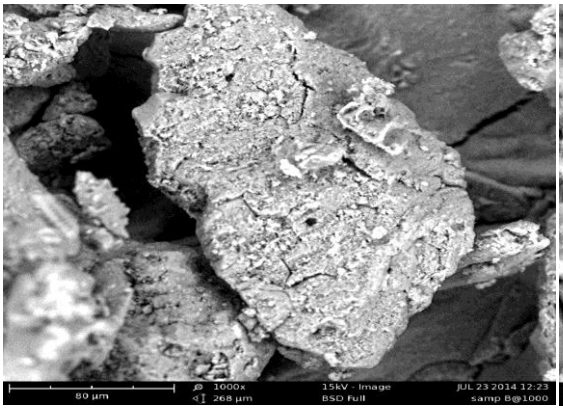
The analysis of microscopic images obtained with a Phenom Pro X Scanning Electron Microscope operating at 15kV is given here. The SEM images presented in Fig 4.12 (a-e) were observed at magnifications of 1000X and 8000X **.**



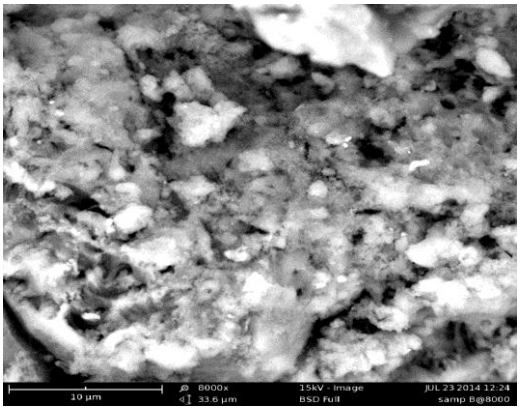
SAMPLE A AT 1000X



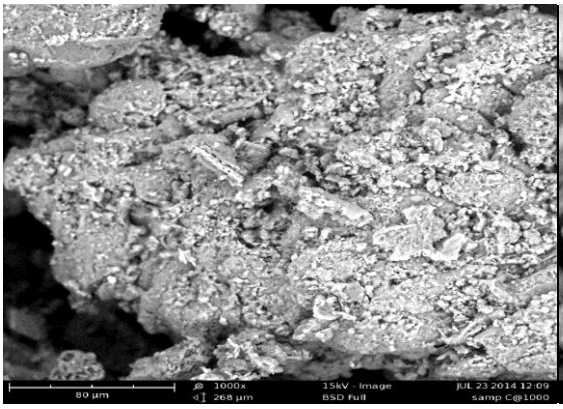
SAMPLE A 8000X



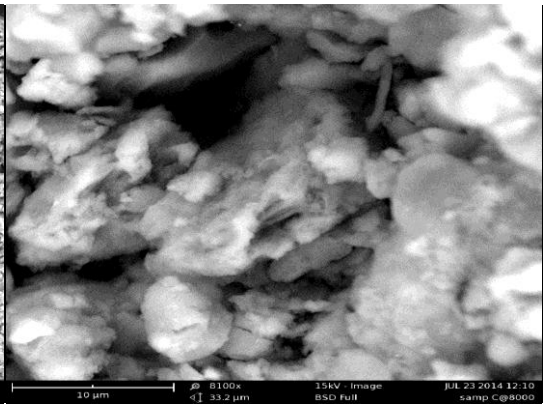
SAMPLE B AT 1000X



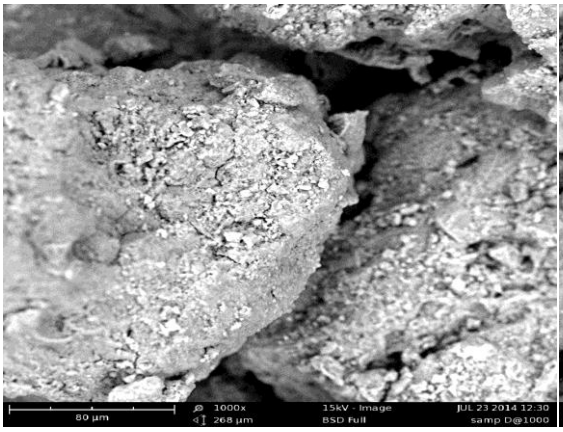
SAMPLE B AT 8000X



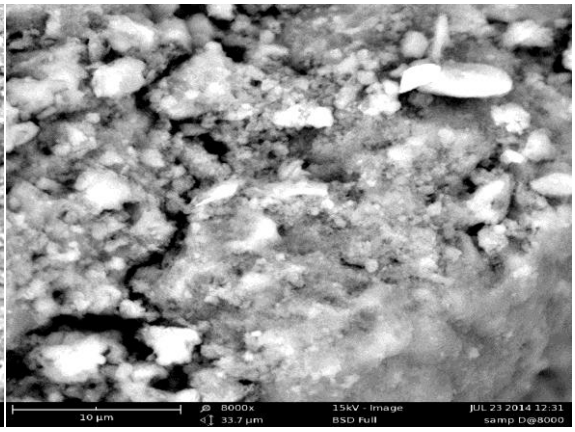
SAMPLE C AT 1000X



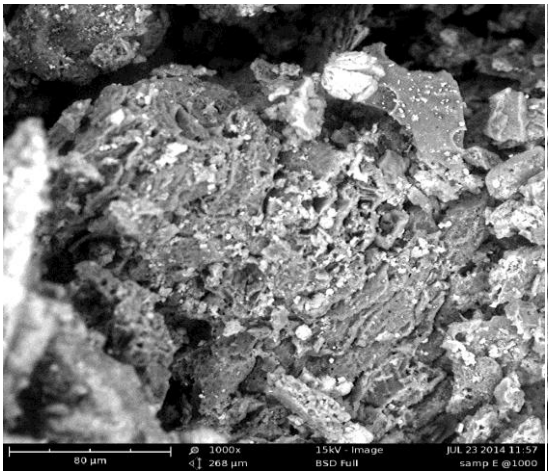
SAMPLE C AT 8000X



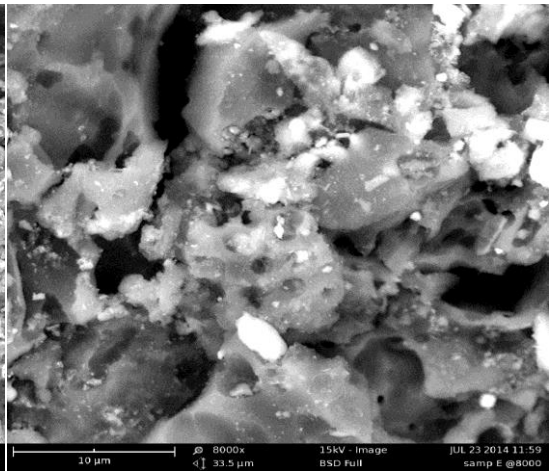
SAMPLE D AT 1000X



SAMPLE D AT 8000X



SAMPLE E AT 1000X



SAMPLE E AT 8000X

Figure 4.12 SEM micrographs of (10000X and 8000X) of samples A-E

4.3.1 Microstructural Analysis

The surface morphologies of activated carbon produced was determined using SEM. Figure 4.12 shows the SEM photograph of Samples A to E at 500X and 1000X magnifications,

The surfaces of Sample A shows some rock like structures with the presence of some transport arteries with cracks and crevices with little sight of pore spaces. Sample B shows some transport pores and smooth surfaces with more visible micropores. Sample C has very few transport pores and little agglomeration, which will not be very viable for adsorption. Sample D can be observed to have some rock-like structures and more transport pores, serving as pathways for the adsorbates to enter the mesopores and micropores. Sample E gives a clearer pore structure, having more volume of pores and better pore structures with little agglomeration, making it more viable for adsorption and thus, the better the pore structure, the better its adsorption capability.

The use of an organic acid and base is tied to enhancement of the surface area. While on the other hand, the substitution of sodium chloride with calcium chloride in the AC is tied to the improvement of the pore structure.The pores seen in Samples D and E are as a result of the evaporation of the activating agents during carbonization and washing after activating, leaving empty spaces. In contrast, as observed from sample A to C, the poor structures can be attributed to improper washing of the activated carbon in which some of the activating agents were not completely removed.

4.4 ELEMENTAL COMPOSITION

Results of Energy Dispersive X- ray analysis for the different composition selected for this study is discussed herein. In table (4.15), it can be observed that the elements carbon,

calcium, chlorine and sodium were seen which is in agreement with the samples that were prepared of which the highest percentage weight of all the elements is carbon. Also, it can be seen that the percentage weight of sodium and calcium in the samples vary of which there tend to be more of calcium than sodium even after washing with distilled water. In addition, the existence of silicon which is a trace element as evident in its percentage weight could be attributed to its attachment to the palm kernel and coconut shells during sample preparation. The potassium element observed is also a trace element from the calcium chloride during preparation from the manufacturers as was seen in the calcium chloride bottle. This can be clearly seen in their percentage weight and atomic percentage. A couple of journals; Volodymyr *et al.*,2009,Journal of Physical Science 2008, Vol. 19(2), 93–104, have results similar to the ones obtained in this experiment where the main elements seen were also Carbon and Oxygen and the trace elements were also attributed to precursor preparation procedure.

Table 4.15 Elemental Analysis of Prepared Activated Carbons

	Sample A	SampleB	SampleC	Sample D	Sample E
Elem	At %	At %	At %	At %	At %
C	79.42	90.94	78.77	88.08	82.08
O	19.06	0.52	17.07	12.87	4.69
Cl	1.01	5.37	2.49	4.88	6.40
Ca	0.50	3.17	1.46	2.21	6.83
K	NA	NA	0.21	NA	NA
Na	NA	NA	NA	0.74	NA
Si	NA	NA	NA	0.32	NA

Total100.00

Where NA indicates not available.

4.5 X-RAY DIFFRACTION ANALYSIS

The samples were characterized using X-ray Diffractometer (Philips X'pert X-ray Diffractometer) employing 1.5046 Å copper source. The samples were scanned from 2θ= 10 – 90°. The value of the interplanar spacing between the atoms, **d** was calculated using the Bragg equation;

$$n\lambda=2d\sin\theta \quad (3.7)$$

where n=1 is an integer, λ is the wavelength of the x-rays, d is the spacing of the planes of the atoms and θ is the angle of incidence of x-ray beam.

The powder diffraction data for the 5 samples are given graphically. Figure 4.13 (A-E) shows the XRD patterns of the samples.

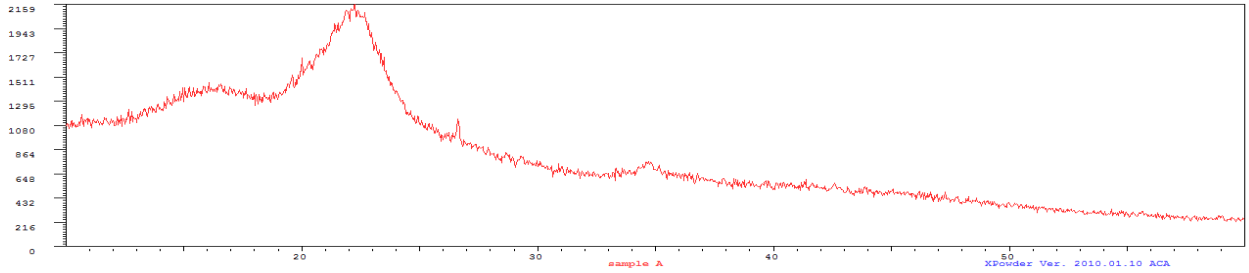
A weak diffraction peak 26.5° was observed in figure 4.13 A,shows values close to that obtained by *Nirmala et. al., 2011* whose diffraction peak was observed at 24.5°, corresponding to (222) $CaCl_2$ plane which corresponds to $CaCl_2$.

Sample B and C do not show diffraction peaks.

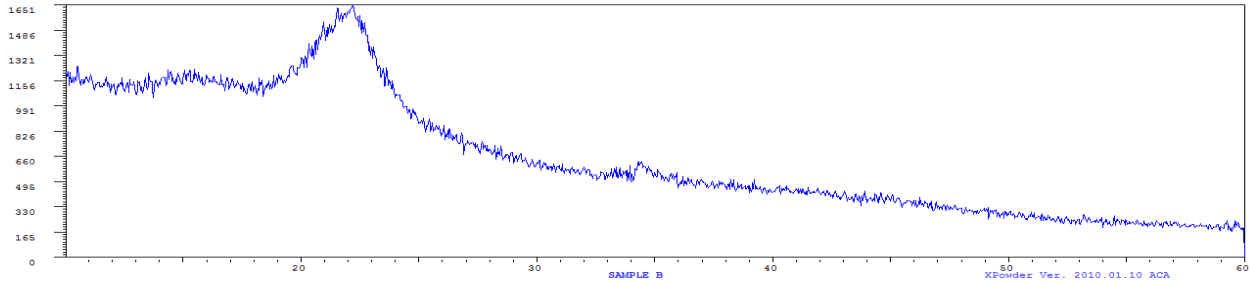
In figure 4.13 D, two peaks at 2 theta 31.5° and 45.0° are observed in the diffraction pattern which has similar values as those obtained by *Arrieta et. al., 1999,* whose values NaCl were of 31.7° and 45.6° and recorded that these peaks correspond to the (200), and (220) reflections.

In fig. 4.13E, a sharp peak, this corresponds to $CaCl_2$, in which the sample had its highest concentration of $CaCl_2$ (as seen in the sample preparation), was observed at 26.5°. Also, the two peaks that were seen in Sample D were also observed in sample E.

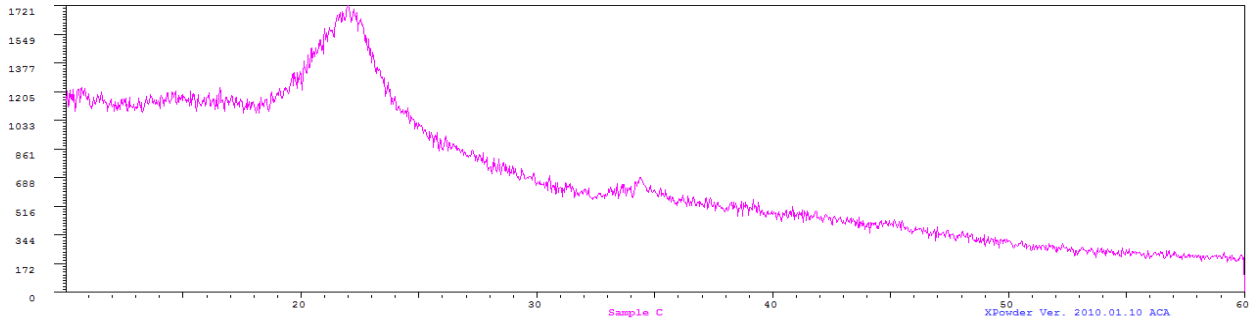
A



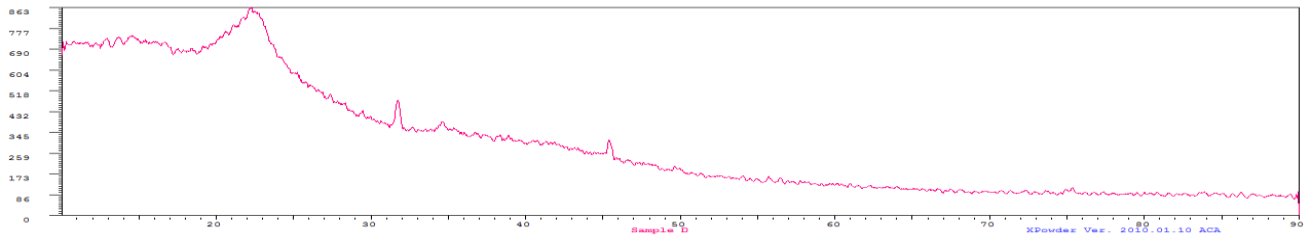
B

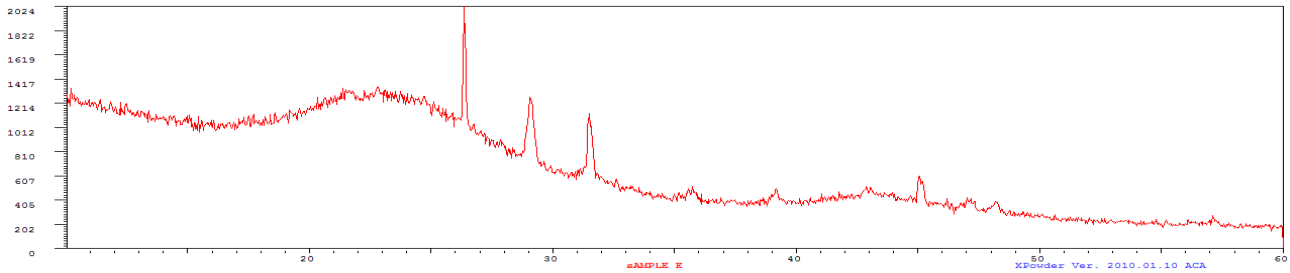


C



D





E

Figure 4.13; XRD patterns for activated carbon with varying concentrations of Sodium Chloride and Calcium Chloride.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In this study, palm kernel shell and coconut shell are impregnated with varying concentrations of NaCl and $CaCl_2$ as activating agents, and activated by microwave radiation at full power (700W) to produce activated carbon. The variation of the impregnation ratio of NaCl and $CaCl_2$, have significant effects on the adsorption capacity of the activated carbon from the prepared samples. Therefore the optimum conditions were obtained as following: impregnation time of 30 minutes, microwave power of 700 W, and a microwave radiation time of 20 minutes.

Activated carbon prepared from palm kernel shell and coconut shell under optimum conditions was employed as an adsorbent for the quantitative removal of methylene blue from aqueous solution. The maximum adsorption capacity for MB on the prepared activated carbon was reached after 30minutes for the sited dye by Sample E and was 333.33 mg/ g. The equilibrium data fitted well in the Langmuir model of adsorption. It was influenced by microwave radiation power and microwave treatments. Development of the porosity of activated carbon was affected by the Microwave power and the presence of activating agents for impregnation.

In SEM, Sample E gives a clearer pore structure, having more volume of pores and better pore structures with little agglomeration, making it more viable for adsorption in comparison with the other prepared samples. In XRD characterization, the presence of irregular patterns of X-Ray diffractograms may be accounted for amorphous state of the samples. A sharp

peak, which corresponds to $CaCl_2$, was observed at 26.5° and also, sharp peaks corresponding to NaCl, were observed at two theta 31.5 and 45.0° in Sample E. The characterizations of the activated carbon produced in this experiment (SEM-EDX, XRD) and ability to remove methylene blue reveals that Sample E produced the best activated carbon as seen from the results, and had an improved adsorption behavior compared to the other samples (samples A-D). Consequently, the activated carbons produced from palm kernel and coconut shell can be used as adsorbents for various environmental applications including treatment of drinking water, removing colour from industrial effluents and removal of heavy metals. It can also be seen that $CaCl_2$ is a very good activating agent judging from the fact that Sample E, having the highest adsorption capacity, was impregnated with more of $CaCl_2$ than NaCl.

The present study concludes the combination palm kernel shell and coconut shell is a very good adsorbent due to its microporous structure comparing its adsorptive capacities with others obtained from others from literature and that microwave heating could shorten processing time significantly and could create porous materials presumably due to its homogeneous structure heating. The prepared samples could be employed as low-cost adsorbents for the removal of dyes and/or impurities within the size range of 1.5nm from wastewater, in general and for the removal of MB, in particular.

5.2 RECOMMENDATION

Based on the result, the following are recommended.

- Investigation on effect of varying impregnation time and activation temperature on adsorption performance should be carried out

- Other chemical activating agents should be tested in order to diversify the activating agent that can be use for chemical activation
- The prepared samples should be employed for removal of impurities in water
- Surface area and pore volumes should be determined for the prepared samples

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APPENDIX

Table 4.2: Table prepared using Freundlich equationfor data obtained from Sample A

S/N	Initial conc. C_o(mg/L)	Final conc. C_e(mg/L)	Log C_e	$q_e = \frac{C_0 - C_e}{m} \times V$ (mg/g)	Log q_e
1	10	7.65	0.8837	117.5	2.0700
2	20	16.22	1.2101	189.0	2.2765
3	30	24.40	1.4048	230.0	2.3617
4	40	35.34	1.5482	233.0	2.3674

Table 4.3: Table prepared using Freundlich equation for data obtained from Sample B

S/N	Initial conc. C_o(mg/L)	Final conc. C_e(mg/L)	Log C_e	$q_e = \frac{C_0 - C_e}{m} \times V$ (mg/g)	Log q_e
1	10	7.99	0.9025	100.5	2.0022
2	20	18.10	1.2577	95.0	1.9777
3	30	26.66	1.4259	167.0	2.2227
4	40	36.10	1.5575	195.0	2.2900

Table 4.4: Table prepared using Freundlich equationfor data obtained from Sample C

S/N	Initial conc. C_o(mg/L)	Res. conc. C_e(mg/L)	Log C_e	$q_e = \frac{C_0 - C_e}{m} \times V$ (mg/g)	Log q_e
1	10	6.70	0.8261	165.0	2.2175
2	20	15.54	1.1875	230.0	2.3617
3	30	24.80	1.3945	260.0	2.4150
4	40	34.70	1.5403	265.0	2.4232

Table 4.5: Table prepared using Freundlich equationfor data obtained from Sample D

S/N	Initial conc. C_o(mg/L)	Res. conc. C_e(mg/L)	Log C_e	$q_e = \frac{C_0 - C_e}{m} \times V$ (mg/g)	Log q_e
1	10	6.40	0.8062	180.0	2.2552
2	20	16.10	1.2068	195.0	2.2900
3	30	25.40	1.4048	230.0	2.3617
4	40	35.40	1.5490	230.0	2.3617

Table 4.6: Table prepared using Freundlich equationfor data obtained from Sample E

S/N	Initial conc. C_o(mg/L)	Res. conc. C_e(mg/L)	Log C_e	$q_e = \frac{C_0 - C_e}{m} \times V$ (mg/g)	Log q_e
1	10	5.50	0.7404	225.0	2.3522
2	20	14.90	1.1732	250.0	2.3979
3	30	24.40	1.3873	280.0	2.4472
4	40	34.42	1.5340	290.0	2.4624

Table 4.7: Table prepared using Langmuir equationfor data obtained from Sample A

S/N	Initial conc. C_o(mg/L)	Res. conc. C_e(mg/L)	$q_e = \frac{C_0 - C_e}{m} \times V$ (mg/g)	C_e/q_e (g/L)
1	10	7.65	117.5	0.0651
2	20	16.22	189.0	0.0858
3	30	24.40	230.0	0.1061
4	40	35.34	233.0	0.1517

Table 4.8: Table prepared using Langmuir equationfor data obtained from Sample B

S/N	Initial conc. C_o(mg/L)	Res. conc. C_e(mg/L)	$q_e = \frac{C_0 - C_e}{m} \times V$ (mg/g)	C_e/q_e (g/L)
1	10	7.99	100.5	0.08
2	20	18.10	95.0	0.19
3	30	26.66	167.0	0.16
4	40	36.10	195.0	0.19

Table 4.9: Table prepared using Langmuir equationfor data obtained from Sample C

S/N	Initial conc. C_o(mg/L)	Res. conc. C_e(mg/L)	$q_e = \frac{C_0 - C_e}{m} \times V$ (mg/g)	C_e/q_e (g/L)
1	10	6.70	165.0	0.05
2	20	15.40	230.0	0.07
3	30	24.80	260.0	0.10
4	40	34.70	265.0	0.13

Table 4.10: Table prepared using Langmuir equationfor data obtained from Sample D

S/N	Initial conc. C_o(mg/L)	Res. conc. C_e(mg/L)	$q_e = \frac{C_0 - C_e}{m} \times V$ (mg/g)	C_e/q_e (g/L)
1	10	6.40	180.0	0.04
2	20	16.10	195.0	0.08
3	30	25.40	230.0	0.11
4	40	35.40	230.0	0.15

Table 4.11: Table prepared using Langmuir equationfor data obtained from Sample E

S/N	Initial conc. C_o(mg/L)	Res. conc. C_e(mg/L)	$q_e = \frac{C_0 - C_e}{m} \times V$ (mg/g)	C_e/q_e (g/L)
1	10	5.5	225.0	0.02
2	20	14.90	250.0	0.06
3	30	24.40	280.0	0.09
4	40	34.20	290.0	0.12

Table 4.12: Freundlich constants for the adsorption of methylene blue on prepared activated carbon

S/N	Samples	R^2	1/n ($L.g^{-1}$)	N	K_f ($mg.g^{-1}$)
1	Sample A	0.94	0.47	2.1336	47.59
2	Sample B	0.68	0.46	2.1987	34.52
3	Sample C	0.95	0.30	3.3378	96.34
4	Sample D	0.89	0.16	6.3816	132.62
5	Sample E	0.97	0.14	6.9979	276.69

Table 4.13 Langmuir constants for the adsorption of MB on prepared activated carbon

S/No	**Samples**	**R^2**	**1/ Q_0 ($_{g.mg}^{-1}$)**	**Q_0** ($mg.g^{-1}$)	**b ($L.mg^{-1}$)**
1	Sample A	0.978	0.003	333.33	0.080
2	Sample B	0.548	0.003	333.33	0.037
3	Sample C	0.999	0.003	333.33	0.158
4	Sample D	0.998	0.003	333.33	0.176
5	Sample E	0.993	0.003	333.33	0.750

Table 4.14; $q_e$and$C_e$values of Samples A- E

q_eA (mg/g)	C_eA(mg/l)	q_eB (mg/g)	C_eB (mg/l)	q_eC(mg/g)	C_eC (mg/l)	q_eD (mg/g)	C_eD(mg/)	q_eE (mg/g)	C_eE(mg/l)
117.5	7.65	100.5	7.99	165.0	6.70	180.0	6.40	225.0	5.5
189.0	16.22	95.0	18.10	230.0	15.40	195.0	16.10	250.0	14.90
230.0	24.40	167.0	26.66	260.0	24.80	230.0	25.40	280.0	24.40
233.0	35.34	195.0	36.10	265.0	34.70	230.0	35.40	290.0	34.20