ADSORPTION OF METHYLENE BLUE AND BRILLIANT GREEN DYES UNTO MODIFIED ACTIVATED CARBON PREPARED FROM AGRICULTURAL WASTES

This study intends to investigate the analysis of removal of Methylene Blue (MB) and Brilliant Green (BG) dyes from aqueous solutions by adsorption on modified activated carbon prepared by chemical activation of coconut shell, eucalyptus tree, corn cob and flamboyant pod. The maximum percentage methylene blue removal was obtained as 95.0% for coconut shell, 93.2% for eucalyptus tree, 99.9% for corn cob and 99.7% for flamboyant pod with all adsorbent dosage at 5g per 0.003mL. Also, the maximum percentage brilliant green removal was obtained as 97.0% for coconut shell, 98.2% for eucalyptus tree, 99.6% for corn cob and 99.6% for flamboyant pod with all adsorbent dosage at 5g per 0.003mL. The adsorption isotherms of the adsorption process were studied and Freundlich model showed the best fit with equilibrium data. To optimize the operating conditions, the effects of contact time, adsorbent dosage, and pH were investigated by two level factorial experimental design method; adsorbent dosage was found as the most significant factor, lower than 95% confidence level with P = 0.0008 for Methylene Blue and P = 0.0069 for Brilliant Green. The obtained results are very promising since the utilization of these agricultural wastes activated carbon used in this work played a critical role in the adsorption of dyes.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the study

The release of dyes into wastewaters from textile, cosmetic, paper and coloring industries poses serious environmental problems (El-Qada, Allen and Walker, 2008). Dye presence in wastewater poses problems in a number of ways. Dye availability in water, even if it is just small in quantity is unwanted and highly visible. Color prevents the proper entrance of sunlight into water bodies; it also retards photosynthesis; hinder the growth of aquatic biota and affect the solubility of gas within the water bodies in water bodies. Dyes role in connection with several lung, skin and many other respiratory problems have been reported globally (Jadhav, Phugare, Patil and Jadhav, 2011). Direct release of dyes containing wastewater into municipal environment can cause the production of poisonous carcinogenic products. The highest degrees of toxicity were discovered in diazo direct and raw dyes (Gupta, Mittal, Malviya and Mittal, 2009). Therefore, before wastewater is released into municipal environment, it is very important to reduce dye amount or concentration present in it.

The commonly applied methods of treating wastewater are coagulation and flocculation, electrochemical treatment, liquid–liquid extraction, chemical oxidation and adsorption. Many methods have recently been used to remove both MB and BG from industrial effluents. Among these methods, Adsorption is the most effective way for the removal of organic compounds from solution in term of its low cost of operation, ease of design, sensitivity to poisonous materials and simplicity of operation (El-Qada, *et al.*, 2008). But its use is limited because of high cost and associated problems of regeneration and this problem has initiated a constant and continuous search for cheaper substitutes. Adsorption process make use of carbons. Wide varieties of high carbon content materials such as wood, coal, peat; nutshells, sawdust, bones, husk, petroleum coke and others have been utilized to produce activated carbon of varying efficiencies (Ponnusami, Krithika, Madhuram and Srivastava, 2007). These materials, usually in irregular and bulky shapes, are always adjusted to exhibit the desired final shapes, roughness and hardness.

Generally, the production of activated carbon involves pyrolysis or carbonization and activation as the two main production processes (Bonnamy, 1999). Numerous carbonaceous materials, particularly, those of agricultural base, are being investigated to possess potential as activated carbon. The suitable ones have minimum amount of organic material and a long storage life. Similarly they consist of hard structure to maintain their properties under usage conditions. They can be obtained at a low cost. Some of the materials that meet the above conditions have been used, in past works, to produce activated carbons which were subsequently used for the treatment of wastewater and adsorption of hazardous gases. Agricultural by-products like rice straw, soybean hull, sugarcane bagasse, peanut shell, pecan shell and walnut shells were used by Ponnusami *et al.* (2007) to produce Granulated Activated Carbons (GACs). The choice of a particular material for the production of effective adsorbent (activated carbon) is based on low cost, high carbon and low inorganic content. Agricultural materials have attracted the interest of researchers for the production of adsorbents because of their availability in large amount and at a low cost (Foo and Hameed, 2011). The selected materials employed in this study were coconut shell, corn cob, flamboyant pod and eucalyptus tree. Use of agricultural by-product for the production of activated carbon is primarily for economic and ecological advantages (Foo *et al*., 2011).

Commercial activated carbon used in surface and wastewater treatment is largely derived from coal. The advantages of coal-based carbons can be seen in their ability to remove toxic organic compounds from industrial and municipal wastewater and potable water as well.

Another significant application of coal-based carbons is decolorization. The feedstock for these carbons, usually bituminous coal, is a non-renewable resource. The long-term availability of coal and its long-term environmental impact coupled with its potentially increasing cost has prompted researchers to consider renewable resources such as agricultural by-products as an alternative. Many efforts have been made to use low cost agro waste materials in substitute for commercial activated carbon (Crini, 2006). Some agro waste materials studied for their capacity to remove dyes from aqueous solutions are coir pith, pine sawdust, tamarind fruit shell, bagasse, rice husk, orange peel, palm kernel shell, cashew nut shell and wall nut shell, (Mittal, Kaur and Mittal, 2008). The present investigation is an attempt to remove Methylene blue and Brilliant green from synthetic wastewater by adsorption process using a low cost activated carbon prepared from agricultural wastes as an adsorbent. The coconut shell and corn cob are considered as an agricultural wastes, therefore using them as raw materials for production of activated carbon is more economical than the coal based activated carbon. In this study, the carbon adsorption method will be investigated for its efficiency in colour removal from water bodies.

1.2 Statement of the problem

The presence of organic pollutants compounds such as dye in water causes serious problems due to their toxicity, suspected carcinogenicity and adverse effects on the human nervous system that cause many health disorders. Removing these contaminants from water is a significant challenge because of ever-increasing pollution of drinking water, the shortage of high quality fresh water and frequent release of wastewater by production companies into water body.

1.3 Aim and objectives

The aim of this project is to remove methylene blue and brilliant green dyes from synthetic wastewater using modified carbons made from agricultural wastes. This aim can be achieved through the following objectives:

1. To carry out characterization of adsorbent by Raman Spectroscopy (RS) and Brunauer-Emmet-Teller (BET).
2. To study the interaction of the mixture of methylene blue and brilliant green dyes on the adsorption sites of the activated carbon.
3. To study the main and interaction effects of the parameters used for the experiments on adsorption process
4. To study the percentage removal of the adsorbents and compare results by measuring the percentage of color remove.
5. To determine the isotherm model where equilibrium data of the adsorption mechanism will be best represented using modified activated carbon.

1.4 Scope of the study

This project investigates the adsorption capacity of four different activated carbons prepared from low cost agricultural wastes on the removal of dyes from aqueous solution. The pH, contact time and carbon dosage effects as well as the interaction nature of the mixture of methylene blue and brilliant green on the adsorption sites of activated carbons will be investigated. Adsorption equilibrium data will be determined. This data will be subjected to

Freundlich and Langmuir models to determine isotherm models that will be most appropriate for equilibrium. This work will be experimental, Raman Spectroscopy (RS) will be used for determination of functional groups present in the carbons and Brunauer-Emmet-Teller (BET) will be used to determine the adsorption capacity of the carbons.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Origin of dye

A dye is a colored substance. It has an affinity to the substrate to which it is being applied. Both stain and dye appear to be colored because they absorb some light wavelengths of more than others. Dyed flax fibers were first found in the Republic of Georgia dated back in a primitive cave to 36,000 BP (Zollinger, 2003). Archaeological proof reveals that, particularly in Phoenicia and India, dyeing has been broadly carried out for over 5,100 years. Different forms of dyes were obtained from vegetable, animal or mineral origin, with little to none processing. The plant kingdom has been greatest source of dyes. Much dyes has been from, notably barks, berries, leaves, and wood, but only few of the dyes obtained from the plant kingdom have ever been used on a commercial scale (Gessner and Mayer, 2002).

2.2 Dyes types

2.2.1 Natural dye

Many of the biological or natural dyes are from plant kingdoms – barks, fungi, lichens, berries, leaves, and wood. Fabric dyeing dates back to the Neolithic time. From the time past, people have dyed their fabric by locally, common available materials. dyes that produced permanent and brilliant colors such as brilliant green, the natural invertebrate dyes and crimson kermes were highly treasured items in the ancient time and feudal world. Plant source-based dyes such as indigo, madder and saffron were good for commercial and economies development in Asia and Europe. Across Africa and Asia, patterned Textiles were produced by dyeing techniques to control the absorption of stain in piece-dyed fabric. Before the end of 19th century, man- made synthetic dyes were discovered. The discovery of man-made synthetic dyes ended the large-scale market for natural dyes to countries around the world. As at today, there are over 10,000 historical collection of dyes at Technical University, Dresden, Germany (Zollinger, 2003).

2.2.2 Synthetic dye

The first man-made (organic) synthetic dye, mauveine, was discovered by William Henry Perkin in 1856. After the discovery of mauveine, many thousands of organic dyes have since been prepared. The natural dyes were quickly replaced by the organic dyes in many applications. Synthetic dyes cost less, they imparted better properties to the dyed materials and they offered a vast range of new colors. Presently, dyes are classified according to their usefulness in the dyeing process, they include (Zollinger, 2003):

- Acid dyes are water-soluble anionic dyes that can be applied to color fibers such as nylon, wool, silk and modified acrylic fibers using neutral to acid dye baths. Most synthetic food colors fall in this category.
- Basic dyes are water-soluble cationic dyes that are applicable mainly to acrylic fibers, but can also find application and use for wool and silk. Acetic acid is usually added to the dye bath to help the absorption of the dye onto the fiber. Basic dyes are useful in the paper making industries for coloration. MB with molecular formula $C_{16}H_{18}N_3SCl$ and BG with molecular formula $C_{27}H_{33}N_2.HO_4S$ are both basic dyes
- Direct dyeing is usually carried out in an alkaline dye bath with the addition of either sodium carbonate (Na_2CO_3) or sodium chloride (NaCl) or sodium sulfate (Na_2SO_4). Direct dyes are also used on silk, cotton, paper, leather, and nylon. They can be used as biological stains or as pH indicators.

- Vat dyes are insoluble in water and incapable of dyeing fibres directly. But, reduction of vat dyes in alkaline liquor produces the water soluble alkali metal salt of the dye.
- Reactive dyes utilize a chromophore that make it good at reacting with fibres substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. Reactive dyes are very easy to use because the dyes can be applied at room temperature. Reactive dyes are best for dyeing process at home, industries or in the art studio.
- Food dyes are classed as food additives, they are use is usually controlled by strictly legislation and they are usually manufactured to a higher standard than some industrial dyes. Food dyes can be vat, direct and mordant dyes. Many azo dyes, such as triphenylmethane and anthraquinone compounds are used for colors such as green and blue (Gessner and Mayer, 2002).
- Other important dyes include: leather dyes for leather, oxidation bases, for mainly hair and fur, solvent dyes, for wood staining and producing colored lacquers, solvent inks, colouring oils, waxes.

2.3 Origin of activated carbon

Activated carbon existence can be traced back to 1500 B.C in Egypt (Pope, 1999). At that time, AC application is limited to medicinal application only, but in the 21st century, AC application is numerous. It can be used to do many things among which water treatment is included. Across the world now, several water treatment plants make use of activated carbons in their water purification to remove taste and odor associated with water. And the present popularity and large number of AC application in water treatment is due to the fact that it treats different problems effectively. Early applications of adsorption involved only purification, for example, adsorption with charred wood to improve the taste of water has been known for at least five centuries. Adsorption of gases by a solid charcoal was first described by C.W. Chele in 1773. Commercial applications of bulk separation by gas adsorption began in early 1920s, but did not escalate until the 1960s, following the invention by Milton of synthetic molecular sieve zeolites, which provide high adsorptive selectivity. Later the pressure swing cycle of Skarstrom, which made possible the efficient of operation of a fixed bed cyclic gas adsorption process.

Activated carbon is probably the most common adsorbent. They are highly porous, amorphous solids consisting of micro crystallites with a graphite lattice. They are non-polar and cheap. Under an electron microscope, the structure of the activated carbon looks a little like ribbons of paper which have been crumpled together, intermingled with wood chips. There are a great number of nooks and crannies, and areas where flat surface of graphite-like material run parallel to each other, separate by only a few nanometers or so. These micropores provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously. Activated carbon can be manufactured from carbonaceous material, including coal, wood, nutshells and coconut shells. The manufacturing process consists of two phases, carbonization and activation (Bonnamy, 1999). The immense capacity for adsorption from gas and liquid phases make activated carbon a unique material. It occupies a special place in terms of producing a clean environment involving water purification as well as separations and purification in the chemical and associated industries. In these roles, it exhibits a remarkable efficiency as the international production is a little more than half a million tonnes per year, with perhaps 2 million tonnes being in continuous use. This is equivalent to the allocation of 200 mg per person of the world population to be compared with the world use of fossil fuels of 2 tonnes per person of the world population. An effective use of activated carbon requires knowledge about the structure of its porosity, obtained from equilibrium data, namely the pore-size distributions of the microporosity in particular, of the pore-size distributions of the mesoporosity, of the composition of the carbon surfaces onto which adsorption occurs, and knowledge of the dynamics of adsorption to indicate its effectiveness in industrial use. Central to activated carbon is the activation process which enhances the original porosity in a porous carbon.

Activation uses carbon dioxide, steam, zinc chloride, phosphoric acid and hydroxides of alkali metals, each with its own activation chemistry. The story of what happens to a molecule of carbon dioxide after entering the porosity of carbon at 800 °C leading to the eventual emergence of less than two molecules of carbon monoxide is fascinating and talks about "atomic ballet”. AC is an adsorbent that can be used to perform functions such as water treatment, air treatment and mixture of gases separation. To activate a carbon, activation process must be carried out, which could be thermal or chemical. Activation by selective gasification (steam or CO_2) in the absence of oxygen to remove carbon atoms is thermal activation while activation that involves the use of some chemicals such as zinc chloride or phosphoric acid is chemical activation. Activated carbon could be made from agricultural waste and other carbonaceous materials such as coconut shell, wood, orange peels and synthetic macromolecular. Not all natural carbonaceous materials are good material for making commercial attractive activated carbon. Past researchers have shown that only few of NOMs provide commercially acceptable activated carbon. Another fact we need to know is that not all activated carbon look very similar to each other or one another even if they are make from the same materials. The reason for this is because of different production conditions. There are many commercially attractive AC available, even some are made from the same materials but with different sizes of porosity due to activation process applied with specific applications. The porosity plays a major role in determining the adsorption capacity of an activated carbon (Gregg and Sing, 1982)

2.4 Activated carbon as an adsorbent

Some solids have capacity to attract some impurities on their surface, but only few of these solids materials have industrial or commercial level adsorption capacity to adsorb adsorbate molecules (Lopez-Gonzalez, Martinez-Vilchez and Rodriguez-Reinoso, 2008). The adsorbate that can be adsorbed may be organic compounds such as odor, taste and color. There are for major known adsorbents in the market today. Each one of them has different characteristics that made them to be different from one another. They are

1. **Silica gel** : it is hydrophilic in nature, it can be used in drying of gas stream but it has an disadvantage of not being able to remove trace substance effectively
2. **Activated alumina:** it is hydrophilic in nature, it can be used in drying of gas stream but it has an disadvantage of not being able to remove trace substance effectively
3. **Zeolites:** it is hydrophilic in nature, it can be used in air separator
4. **Activated Carbon:** it is hydrophobic in nature, it favour organics over water. It can be used in removal of organic pollutants. Its only disadvantage is that, it is always difficult to regenerate for re-use.

2.5 Uses of activated carbon

There are several operations where AC is applicable today for impurities treatments, these include

1. AC can be used in biological primary and secondary processes, physio-chemical treatment to obtain purify effluent.
2. AC can be used for tertiary AC processes on wastewater that has already undergone either primary or secondary biological treatment process. This will result in effluent of about 99% purity. Tertiary treatment is adsorption which could be batch or fixed bed treatment.
3. AC is also applicable for industrial waste treatment for either pre-treatment of effluents before discharge into rivers, streams or municipal treatment plants or to upgrade the wastewater for re-use.
4. AC can be used to purify water by removal of biodegradable, chemicals, oil and other organic compounds that are not responsive to conventional biological treatment. Biological treatment may include addition of lime, alum, chlorine, followed by filtration.
5. AC can be used to treat wastewater that contain pesticide, polyols, detergents, phenols and organic dyes.
6. AC can be used to treat wastewater and effluents from pulp and paper mills, fertilizer plants, fabric dyeing, rubber tread factories, chemical and pharmaceutical factories etc.
7. AC can be used to remove oil from wastewater or effluents.

2.6 Adsorbent and adsorbate peculiarity

Today, there is thousands of AC in the market that can be used to treat water related problems, but before a particular AC is picked, there are some factors which will enable adsorption on AC during water treatment. They include

1. Water pH, quality and ionic strength
2. The shape, size, charge, solubility, hydrophobicity of adsorbate
3. Surface chemistry and pore size of AC

The removal of target impurities can be achieved by the interaction of all the listed factors above. The carbons most suitable for adsorption are the ones that has a large volume of pores in size range slightly larger than the adsorbate. AC surface chemistry is very important in adsorption process and all the other factors. Researches on adsorption have tried to proof that the adsorption of a particular contaminants are related to the pore volume and surface chemistry. This means that the adsorbate on a particular AC can be adsorbed depends on pore volume and surface chemistry and these can be different from one laboratory to another. (Gonzalez, Gonzalez, Molina-Sabio, Rodriguez-Reinoso and Sepulveda- Escribano, 1995).

2.7 Regeneration of activated carbon

By the time AC or adsorbent has become saturated then it can be either discarded or regenerated. But for regeneration, saturated carbon will be removed from adsorption column in the form of a slurry. The slurry (the semi-mixture of used up AC and water) will be dewatered, and passed into the furnace for heating. Regeneration is always done by thermal process and is a reversible process. Inside furnace AC is heated under controlled conditions with no or little oxygen content to avoid carbon burning on combustion. The heating process evaporates out organic compounds the adsorbent adsorbed during adsorption and also removes residual water in the adsorbent. After the heat treatment is completed, the carbon is cooled with water, wash and dry in the oven and recycled for adsorption process reverse. The regeneration can be off-site or on-site activities. During regeneration, some carbon will be burnt-up during the process. About 2 – 10wt% will be burnt-up. For re-use, some fresh carbon will be added to the regenerated carbon to replace the lost carbon during regeneration. The whole process can be done within 30 minutes to one hour. Physical regeneration require high temperature due to this, it is a high energy process that is commercially and energetically expensive process. Plants that use thermal regeneration of activated carbon must be very big and must have adequate facilities on site before it can be economically viable to do so. Due to this most of the activated carbon generation companies usually carry their waste for treatment in specific AC regeneration facility center. Many generation process of AC can be carried out in heating appliances such as toaster or baking ovens. Other regeneration techniques are wet air oxidation, ultrasonic regeneration, microbial regeneration, electrochemical regeneration and chemical and solvent regeneration. The expensive natures of physical regeneration encourage researchers to come up with above listed means of AC regeneration. All the techniques listed apart from physical regeneration can be used as alternative regeneration which could be employed in medium-scale industries

2.8 Activated carbon production

Activated carbon is a carbon produced from carbonaceous source materials. The production methods can either be by thermal activation or by chemical activation.

2.8.1 Thermal activation processes

Natural Organic Material (NOM) can be carbonized (convert into char by heating or burning in the absence of oxygen) to microporous carbons (Gupta, Rastogi, Agarwal and Nayak, 2011). Carbonize materials do not maximize their porous potential, that is, carbon adsorption capacity when measured is too low to be considered useful for commercial application. There is need to widen the exiting porosity to wider micropores and some mesoporosity. Also, because of narrow porosity within the carbon, it is closed to pick up some specific adsorbates (contaminants) inside the water. To allow and increase the capacity of adsorbent to adsorb the adsorbate, porosity and space within the carbon, which is closed must be opened in other to allow access to larger adsorbates molecules. The process of opening the space within the carbon to maximize it adsorption potentials is by activation. The activation process can either be by chemical or physical activation. The first means of widening the porosity make use of steam and carbon dioxide, either singly or both combine. The functions of this gasify agents is to open the space or pores within the carbon by extracting carbon atoms from the structure of the porous carbon. The method describe above is known as physical or thermal modification or activation. The stoichiometric equation for thermal or physical activation is given as

$$C + CO_2 = 2CO \tag{2.1}$$

$$C + H_2O = CO + H_2 \tag{2.2}$$

The second suitable modification or activation process of widening the porosity make use of chemicals such as potassium hydroxide, KOH, zinc chloride, $ZnCl_2$, phosphoric acid H_3PO_4 and potassium carbonate K_2CO_3 (Foo *et al*., 2011). This activation method is known as chemical activation, and the process of widening porosity follow the same as physical activation. Some industrial adsorption processes of widening the space within the carbon usually combine both thermal and chemical activation process together to obtain a desired activated carbon. The mechanism of activation used does not produced identical result. The use of gasifying agents to remove carbon atoms as carbon monoxide which then enhancing space does not give the same result. The result one will get if steam is used for activation is different from that of carbon dioxide.

2.8.2 Chemical activation processes

The chemical activation process consists of mixing a carbonaceous precursor with a chemical activating agent, followed by a pyrolysis stage. The material after this stage is richer in carbon content and presents a much ordered structure and, after the thermal treatment and the removal of the activating agent, has a well-developed porous structure. Different compounds can be used for the activation; among them, KOH, NaOH, H_3P0_4, and $ZnCl_2$ have been reported in the literature to be the best for activation (Gonzalez *et al*., 1997). It has been discovered that chemical activation has some advantages over physical activation. Some of the advantages of chemical activation over the physical process include

I. The chemical activation uses lower temperatures and pyrolysis time,
II. It usually consists of one stage,
III. The yields obtained are higher,
IV. It produces highly microporous ACs
V. It is a suitable method for applying to materials with high ash content.

On the other hand, the chemical activation presents disadvantages such as the need of a washing stage after the pyrolysis and the corrosiveness of the chemical agents used. For time past, active carbon application as adsorbents have been used where impurities in the concentration need to be removed. For active carbon to be effective as adsorbent, it must have an appropriate pore-size distribution and large micropores volume to adsorb molecules of different sizes. Also, to facilitate micropores access, there must be an adequate preparation of mesopores (Gupta *et al.*, 2011). So to meet the broad range of industrial requirement of active carbon, intensive research to provide activation methods is undertaken by different researchers in different laboratories. These researchers are developing methods of activation to develop active carbon with optimum, pore-size distribution that industrial requirement needs. As application become specific, the researchers' are developing active carbon with specific pore-size distribution to meet specific application. This means that not all activated carbons can be used, for the nature of the impurities to be removed will determine active carbon to be used in order to achieve desire result. For example, activated carbon with homogenous microporosity is required to recover light hydrocarbons found in gasoline vapour by adsorption process. So active carbon with homogenous microporosity and controlled pore-size distribution are prepared by controlled activation of precursors (Gonzalez *et al.*, 1997).

To develop a specific microporosity in activated carbon, either thermal or chemical activation process can be used. But in thermal activation, factors such as heating rate and time, temperature, pressure etc, has little influence on micropore size distribution (Gonzalez *et al*., 1997), it may be difficult to control the microporosity development of AC to specific desire pore distribution size. In order to have a control pore – size distribution in AC, chemical activation is an alternative that can be used. In chemical activation, precursors can be well-controlled and modified to prepare activated carbon with specific microporosity. Chemicals such as zinc chloride, H_3PO_4, $CaCl_2$ are commonly used for carbon activation at a temperature of about 723K-873K. At these temperatures, there is always incomplete carbonization and hence the chemical composition of the carbon prepared is between that of the char and precursor. During carbonization process, there is always a contraction in dimensions of precursors. Studies carried out with agricultural waste (Almond shells) showed that the loss in weight of about 75wt% is followed by 30wt% contraction (Gonzalez *et al*., 1997). In chemical activations, change in dimension during carbonization is very necessary. Change in dimension makes reagent to be able to be incorporated into carbon interior where it prevents the expected contraction with increasing temperature. This means that the creation of microporosity can be caused by reagent.

2.9 Factors on which activation depends

The following factors which may influence the properties of an activated carbon were recommended by Gonzalez and co-workers (1997) to include:

1. The time of activation;
2. Activating gas flow rate
3. The equipment used for the experiment.
4. The activation temperature;
5. The activating gas;
6. The parent feedstock;
7. The rate of heating;
8. The flow rate of the containing gas, usually nitrogen

The above listed factors can influence the properties of AC and adsorption capacity. The way the activating gas flow into the bed of carbon, the carbon bed construction and where the bed is located in the furnace are all factors that influence the properties of AC. When comparing results from laboratory to laboratory, some differences are to be expected, even when all the conditions and the listed factors above are fixed (Gonzalez *et al.*, 1997). Gonzalez and co-workers used olive stone to prepared three different chars. The olive stones, 1 – 1.5mm particle size, carbonized with the same conditions namely;

1. Slow carbonization inside horizontal furnace, heating rate 278K min3, N_2 flow rate of 80cm3/min, reaction temperature 1123K, 1 hour of soak time and 25.4wt % of char yield was the result

2. Slow carbonization inside vertical furnace, heating rate 278K min3, N_2 flow rate of 80cm3/min, reaction temperature 1123K, 1 hour of soak time and 26.8wt % of char yield was the result
3. Flash carbonization inside vertical furnace, heating rate 278K min3, N_2 flow rate of 80cm3/min, reaction temperature 1123K, 1 hour of soak time and 16.7wt % of char yield was the result

The chars yield of the three precursors which were prepared under the same experimental factors and conditions are not the same. And one will also expect that their reaction with carbon oxide will also be different. In order to compare the activation carbon adsorption capacity, the same activation process was used for the three chars yield. The activated carbon produced were analyzed using carbon dioxide (273K) and N_2 (77K) isotherms. The results from the point of porosity development showed that there are differences between the two activation methods used. The micropore volume of the chars activated in horizontal furnace are larger compared to that of the vertical furnace. So the horizontal furnace is at the advantage for AC activation. It was observed that the large micropore volume of horizontal furnace is as a result of external mass – transport which is more limited and favour internal gasification of the char particles and the creation of micropores. The conclusion of the study showed that enhancement of micropore volume and adsorption capacity is favoured by horizontal carbon bed than that of vertical carbon bed at the same activation temperature (Gonzalez *et al.*, 1997)

2.10 Comparison of activating agents

Factors such as temperature, activation time, soaking period, nature of the chemical used and the concentration of chemical used are factors that determine the reaction between precursors and chemicals during activation. The research shows that for activating agents such as KOH, $ZnCl_2$, and H_3PO_4 (Gonzalez *et la., 1997),* they always act on carbonized materials to produced activated carbons with micropore volume of 0.4, 0.5 and 0.6 cm^3/g respectively. In chemical activation, chemical react with precursor, but at the end of impregnation, there is always difference which can be observed. Impregnation with H_3PO_4 always make particle to become elastic. Particle become elastic simply means that H_3PO_4 impregnation starts the conversion to carbon process because at the surface of the particle a significant amount of tar is observed. During impregnation with H_3PO_4, some visual changes are observed; there is swelling of the particle, decrease in mechanical resistance and presence of tars on the surface of particles. But with impregnation with KOH, there is no swelling up of the particles, mechanical resistance, and no formation of tar but only a slight dehydrating occurs on particle surface. Impregnation with $ZnCl_2$ followed the nature of impregnation with H_3PO_4. In $ZnCl_2$, there are also visual changes such as swelling of the particle, presence of tars on the surface and lower mechanical resistance. Another thing for comparison is dehydrating effect during heat treatment. Chemical is a liquid at the temperature of the process, this made the dehydration to be possible. Dehydration facilitates the bonding to the precursor being thermally degraded and enable chemical to enter into the interior of the particles. The dehydration produced by KOH is weak and does not seem to affect carbonization but dehydration made by both H_3PO_4 and $ZnCl_2$ is strong. The dehydration produced by phosphoric acid and zinc chloride affects carbonization (Gonzalez *et al*., 1997). Both H_3PO_4 and $ZnCl_2$ yield reaches values up to 45wt% with larger concentration of chemical for $ZnCl_2$ and low concentration for H_3PO_4. The peak yield for KOH was 25wt%, which is the same yield of the precursor un-impregnated with any chemical. The reduction in the dimension of the particle is caused by precursor dehydration, and such reduction is partially prevented because during physical treatment, reactant remains, thus acting as a template for microporosity creation. Also both H_3PO_4 and $ZnCl_2$ act as a dehydrating agent on the precursor, thereby react during pyrolysis. KOH does not produce dehydrating effect on the precursor. It does to prevent the contraction of the particles with heat treatment and does not react during pyrolysis. KOH starts to react with pyrolysis at about 973K. At this temperature precursor changes to char. In activation process with KOH, activation consists of a redox reaction initially. A redox reaction is the reaction where carbon is oxidized to CO_2 or CO, thus creating some porosity and K_2CO_3 is produced as by – product. The conclusion of the work is that H_3PO_4 and $ZnCl_2$ are best activating agents and they always produced similar or better yields of about 26-46wt% compared with physical activation with a yield of about 8wt% (Marsh, Heintz, and Rodriguez-Reinoso, 1997), and that activation by chemical process has some advantages over thermal activation process. $ZnCl_2$ always produce wide pore surface area than base, but H_3PO_4 produces a better pore surface area and are relatively safer than $ZnCl_2$ (Gonzalez *et al*., 1997)

2.11 General considerations on activated carbon

The generation observation and common behavior discovered about most of the activated carbons prepared by physical activation process from different raw materials is that, there is initial increase in micropore volume up to about 20wt% burn off. This increase in micropore volume occurs mainly by widening of existing microporosity and by creation of new microporosity. After the initial increase of 20wt% micropore volume, thereafter, there is increase in micropore volume which is smaller and after 40 – 45wt% burn – off, the micropore volume then progressively decrease, this trend of burn- off shoes that pore enlargement during activation shift from microporosity to mesoporosity and even to macroporosity. The observation also shows that at a high level of burn-off, there is a fierce burning of the exterior of the carbon particle in conjuction with interior of carbon porosity widening. The industrial gasification of any char to open and widen porosity has three mechanisms often carried out to explain how porosity develop during activation of a chair. These mechanisms include

1. Existing pores widening
2. Creation of new pores
3. Opening up of pores that are not accessible previously.

The mechanisms written above make increase in micropore volume (15-20%) for the char activated. There is about 10wt% burn-off which is a good indication of the opening of initial inaccessible microporosity. The removal of reactive carbon atom which is in the form of carbon monoxide for carbon takes place at the activation process initial stage (Rodriguez-Reinoso *et al.*, 1997)

2.12 The porosity of activated carbon

The voids, spaces, sites and pores in activated carbon make it to be a unique material that is filled with holes, the size of the molecules. These pores in activation carbon have a strong force known as Van der Waals which is responsible for the adsorption process. The pore size determines how the adsorption process will take place in activated carbon. The pore sizes range from macroporosity > 50nm, mesoporosity 20 – 50nm, and microporosity < 2nm. The dominant characteristics of adsorption is imparts with porosity within activated carbon. There is a wide range of materials of carbon family that are good for preparing activated carbon of different structure and porosity. The porosity and structure of carbons are prerequisite to the effectiveness of activated carbons. And the origins of parents materials of activated carbons and preparation conditions and methods determines the porosity and structure within AC. Porosity within a porous solid are sites, voids, holes, spaces and pores which is enhance to molecules from liquid phase and gas phase. Carbon which is an adsorbent is a porous solid material, while adsorbate is a solute from solution, gas or vapour which within the adsorbent is adsorbed. The solute, gas or vapour which will be adsorbed as an adsorbate is adsorptive. When an adsorbate enters into the porosity of the adsorbent, then adsorption process takes place.

In adsorption, there are three kinds of entrance into porosity. The entrance dimension of micropore is < 2nm, mesopores is 2 – 50nm and macropore is > 50nm. The entrance dimension from 2 – 50nm and >50nm show that there is a continuous and progressive pattern of adsorption within the AC from structural point of view. For carbon to have specific dimension, there is a specific method of preparation which need to be applied before a carbon with a specific dimension is created. The carbonization of precursor is responsible for the creation of porosity to some degree in a carbon. Porosity of different sizes and the sizes make carbon to be accessible or inaccessible to particles. For example, organic pollutants are accessible to some porosities but inaccessible to organic pollutants. Some are accessible to helium and closed to lithium. For porosity dimension, the nomenclature assigned has been in used for past decades. In recent times, carbons with dimension < 1nm have been called nanoporosity. Ultra micro porosity in literature is suggested to be dimensions of about < 0.7nm as well as dimension nearer to 2nm is called to be super – microporosity. All these names in term of pore radius and diameter can be misleading. But this work concern is on micro and meso- porosity dimension. There is a need to emphasize that adsorption processes in porosity < 0.7 nm are distinct in the way that the intense dispersion forces, which operate in such confined volumes, influence the physical state of the adsorbed phase. It has to be said at the onset that the numerical values attached to these definitions of porosity do not have the precision as is attached to a weight or a volume. Rather, a pore is defined according to the way it adsorbs an adsorbate molecule and that is a function of the size and polarity of the adsorbate molecule as well as the size of the porosity and surface polarity within the adsorbent.

The above discussions have stressed that porosity in this family of carbons essentially is that space where carbon material (atoms and heteroatoms) is absent. If the structure or relative arrangements of carbon atoms is changed in some way then automatically a new set of porous properties will be created. It therefore follows that a knowledge of structure assists with knowledge of the nature of porosity in that carbon. Today, almost all the plants in the world can be used to prepare active carbon on carbonization in an inert atmosphere. But causal preparation of active carbon may not be able to meet requirements for commercial application. Activated carbon for industrial application must be capable of performing efficiently and effectively. The efficiency and effectiveness required in activated carbons have led to extensive research for the development of active carbon for application optimization. Active carbons in the market today are the product of intensive research and development. And both the producers and the users of activated carbons in market must be familiar with pores sizes. This is necessary because consumers need to be familiar with abilities of activated carbons that he/she will buy. The pore dimension of AC determines its functionalities during adsorption. Also the potential user should be acquainted with kind of pore size within the carbon because this determines its application. As activated carbon has so many applications, it is imperative that a detailed knowledge should be available of the nature of the porosity within carbons, and those factors which adsorption process depends on, are those that control the strengths and extent of adsorption. Activated carbon does happen by either chemical of physical activation and carbonization. But porosities that develop by initial carbonization are not sufficiently developed for most of commercially or industrially applications. So, to make them fit sufficiently for commercially or industrially applications, further process of activation must be applied. And this could be chemical or physical activation that help to open up the porosity within the carbon in one of the following ways

1. Opening up of closed pores
2. Creation of further spaces
3. Widening of existing porosities
4. Porosity surface modification
5. Improvement of carbonization process itself.

All these can be done in several ways. All thermal activation processes are heterogeneous reactions which could be carried out by either carbon dioxide or steam or mixture of both gases (Rodriguez-Reinoso *et al*., 1995). In thermal activation, steam or CO_2 gives carbons with different porosities. The process of selective removal of individual carbon atom by steam and CO_2 from carbonized carbon is thermal activation. The stoichiometric chemical equation for gasification process is carbon plus CO_2 gives CO. The temperature range for the process is about 800 – 1000 0C. The reaction kinetic shows that carbon atoms are removed from activated carbon by the effect of steam or CO_2. Literature has revealed that only coals possess the unique capacity as the parent precursor in which AC can be prepared without any initial carbonization, but every other parent materials, will required the initial carbonization for porosity to be developed which may later require activation to develop the porosity to the desires pore volume size (Foo *et al*., 2011). In addition to the main processes of activation by carbon dioxide or steam, three other techniques of chemical activation are used, involving co-carbonization with (a) zinc chloride, (b) phosphoric acid and (c) with potassium hydroxide. Mechanisms for these activations are all different, with zinc chloride promoting the extraction of water molecules from the lignocellulosic structures of parent materials, and phosphoric acid combining chemically within the lignocellulosic structures. There is no selective removal of carbon atoms as during physical activation and carbonization yields are improved. The mechanisms by which potassium hydroxide activates an existing carbon are more complex and involve the disintegration (almost explosively) of structure following intercalation as well as some gasification by the oxygen of the hydroxide. The presence of oxygen is not essential (but may be helpful) to this form of activation.

2.13 Wastewater and water treatment

Water and wastewater can be considered as complex mixtures of suspended solids, colloids, and dissolved organic or inorganic pollutants due to natural discharges or human activities. The contaminant levels are quite low in drinking water sources compared to pollutant concentrations found in industrial wastewater. However, to obtain clean water, several physicochemical or biological processes are available and commonly carried out, such as sedimentation, coagulation, flocculation, filtration, adsorption, oxidation, and free or fixed microorganisms .To control and limit the impact of inorganic species on human health and the environment, treatment processes have to be defined and proposed. The methods for the removal of cations or anions from water are precipitation, membrane processes (nanofiltration or reverse osmosis), oxidation, biotreatments, ion exchange, and adsorption .Activated carbon in the form of powder, grains and, more recently, fibers (cloth or felt) is a universal adsorbent and, in particular, some interactions occur with inorganic species present in water. Literature revealed that the use of carbon in water purification has been in use as back as 4000years. The purpose of using carbon is to remove odor, taste and color in water (McGuire *et al*, 1983). But in this modern day, AC is mainly use for the removal of organic pollutants. These organic pollutant compounds can be divided into three categories, namely

1. Synthetic compounds
2. Natural Organic Materials (NOMs)
3. Water treatment chemicals by-product

Synthetic organic compounds in water can be phenols, toluene, benzene, oil, chlorophenols, Pesticides, dyes, tetrachloride, and so on. AC has the capacity to adsorb all these organic compounds in water. Because of its capacity to remove synthetic organic compounds in water , many water treatment industries are making use of AC to purify potable water. NOMs are residues of living things metabolism. These NOMs are the source taste and odor in water. Finally, trichloromethane is the chemical treatment by-products in water.

For removal of organic compounds and other water contaminants, AC has become a major market in water treatment worldwide for liquid – phase application. AC can be used for primary and tertiary treatment of effluent. The use of AC for water treatment has the highest application .It has almost 50% , follow by waste water treatment which is about 40% application, after the wastewater treatment, the next market for the application of AC is groundwater. Both PAC and GAC are useful in water treatment processes. In batch process, PAC is added to water as slurry, the electric agitator or stirrer is used to mix the slurry. After a suitable contact period, PAC is removed by filtration or clarification. In taste and odor control, dosage of AC depends on the level of impurities and contaminants in water. But the ideal is that AC dosage should be low. PAC is useful in the removal of odor and tastes, toxins cause by blue-green algae. It is also useful in the removal of high level of pesticides and other man-made industrial impurities in water. PAC is always mixed with water to form slurry, and the time that PAC stay in water determines its effectiveness. PAC has a lot of uses that have been written down in the several literatures that are easily obtainable on-line. Generally, PAC are active carbons made in a particulate form as powders or fine granules less than 1.0mm in size with an average diameter between 0.15mm to 0.25mm. Adsorption effectiveness of PAC depends on the correct dosage pour into water to reduce target compounds to the target level of acceptance by the operators. In this modern day, technology such as computer modeling can be used to know specific dosage PAC that will be required to reduce target compounds during water treatment. For adsorption to take place, these four interaction process must take place between adsorbent and adsorbate. They include

1. External mass transfer of the adsorbate from the bulk fluid by convection from to the outer surface of the adsorbent
2. Internal mass transfer of the adsorbate by pore (hole or space) diffusion from the outer surface of the adsorbent to the inner surface of adsorbent internal porous structure
3. Diffusion inside internal pore structure to the most effective adsorption site
4. Adsorption of adsorbate onto AC surface

These four steps is the sequential order by which adsorption always take place during purification processes. For effective prediction of adsorption, a series of experiments must first be carried out using the active carbon that will be eventually use for overall treatment to remove compounds of interest in water or wastewater. This will enable the operator to know the best operation conditions under which treatment process must be carried out to achieve the desire result during treatment.

GAC is also good for odor and taste treatment, but GAC is most useful in water treatment when there are persistent odor and taste problems. GAC is also useful in water purification using special filters and disposable cartridges in residential, industrial and commercial installations. GAC is best useful in fixed bed continuous flow and gravity column in fixed bed, the flow may be up-flow of down-flown system for a set contact time. The removal of used AC in an up-flow system is done from column bottom while addition of new fresh AC is done from the top of column. In down-flow system, suspended solids are accumulated at the top AC bed. And because on the bed there is pressure drop caused the accumulated solids periodic back-washing of the bed is required to relieve the pressure drop on the bed. Down-flow is always operated as either parallel or series during purification process. In down flow system, AC is used up first at the top of the bed and it is always important to remove entire bed in order to replace the carbon. GAC is usually used in liquid-phase and vapour-phase treatment. GAC is designated by sizes such as 20x40, 8x20 or 8x30 for liquid-phase application and 4x6, 4x10 or 4x80 for liquid-phase application. A 20x40 carbon is made of particles that will pass through U.S Standard mesh size No 20sieve (0.42mm). The most common mesh size for GAC is 8x30 or 12x40 sizes. They are common because they have surface area, head loss characteristics and a good balance size.

2.14 Removal of impurities of concern from potable water

AC found a major uses in the removal of chemicals present in water due to human activity. These chemical impurities which includes personal care product, pesticides, pharmaceutical and industrial chemicals that enter water sources through untreated wastewater or re-use of treated wastewater. AC also has another major application in the removal of odor and taste. Though odor and taste have no major health concern, but they become necessary to remove because of frequent complaints by the water consumers and consumers complaints to authorities on water. Another area where AC found every less important uses is removal of blue-green algae toxic metabolites. Toxic metabolites is responsible for range of diseases and illness such as nerve damage, liver damage etc. Toxic metabolites, even when they are present in water in small amount, they are of very great concern to water industry because of potential adverse health effects.

2.15 Industrial and pharmaceutical pollutants

A range of chemical pollutants can found their ways into the source of drinking water. Major chemicals, pharmaceuticals, petroleum etc., industries are sited in cities and places where their wastes or their production materials can easily found their ways into waterways or large rivers. Many of these industries waste materials can also found their ways into water bodies through storm carriage. Some of the chemicals can also found their ways into water bodies or source through accidental spills of chemicals. All these and many other ways by which chemical pollutants can found their ways into the drinking water sources are causing environmental hazard. Though there are many environmental regulations by governments to control chemical pollutants but many are still finding their ways into drinking water sources. These contaminants are s major concern to water suppliers and potable water producers. To remove these chemical from water, activated carbon becomes necessary in purification process for adsorption of these chemicals out of the water. Both PAC and GAC has the ability to remove industrial chemicals in water and today AC has become a widely used adsorbents in the removal of industrial chemical such as methyl-tertiary, butyl-ether, trichloro-ethylene and other chemical from water sources or bodies. Pharmaceutical and personal care products such as antibiotics, shampoos, soaps, moisturizing notions, hormonal medicines and other substances containing phenols, benzenes, phthalates are present in drinking water sources. All these contaminants are the sources of problems in both humans and animals endocrine system disruption. In water industries, aesthetic quality is of great concern. Odor, color and taste are most complaints issue by the consumer of water worldwide. Apart from chlorine which the purpose in water is to ensure microbiological safety, but chlorine at times, may be the source of odor or taste in water, but majority of odor and taste in water are caused by algae metabolites in the water sources. The most rampart and common algae metabolites is 2-Methyl-isoborneol (MIB) and geosmin. Other are cyanobacteria which can produce algae toxins dangerous for health well-being and cause damage to liver, skin irritation, tumor promotion and eventually death.

2.16 Natural organic material removal (NOM)

Activated carbon is not the most effective way for the removal of NOM in water, but when both PAC and GAC are applied with intention to remove NOM, PAC when applied, remove very small quantities when compare to solute concentration in solution. However, the removal power of GAC filters is high when at first insertion. GAC initially can have the capacity to remove between 10% - 20% of NOM at a steady state. The complex nature of NOM has made GAC and PAC not to be able to remove it from water, but even little removal of NOM in water is beneficial to water supplier because it will lower the disinfectant consumption and formation of disinfection by-products. NOM which means natural organic material are dissolved materials which consists of complex mixture of compounds, this make it difficult to have a chemical structure by which NOMs could be identify. With the aid of elemental analyses and spectroscope analyses, humic acid is one of the organic material in NOM. Other include oxygen containing functional group such as hydroxyl, methoxyl, aromatic, and aliphatic. NOM chemical characteristic depends on the source materials and various compounds of the environment biogeochemical process is occurring. NOM is very difficult or impossible to characterize because of its chemical structure is a complex mixture of dissolved substances. Also the complex mixture of NOM has made it very difficult to its effect during adsorption on AC. NOM always compete with micro-contaminants on the adsorption sites of AC. Many test such as ideal adsorbed solution theory (IAST) and equivalent background compound (EBC) model can be used to obtained the parameters that will enable the water industries to know exact dosage of AC that will be effective and specific time of operation that will be enough to remove both NOM and other compounds of target in water to the desire level. Literature has also revealed that NOM is responsible for the GAC fouling when AC adsorption sites are blocked by NOM particles. The surface properties of AC can be charge by NOM particles when NOM adsorb onto the AC causing AC ineffectiveness for adsorption process. NOM has a neutral pH has high negative charge. Drinking water sources have NOM molecular weight ranging from 300 – 400 g/mol.

2.17 Adsorption

The process where van der Waal’s pull out impurities from water bodies and stick them onto the surface of adsorbents is called adsorption. Due to intermolecular surface forces such as the Van der Waals force, molecules attach to the surface of the adsorbent, and energy is released. This is called physical adsorption. Additionally, there may be chemical forces such as ion exchange, causing a chemical bond between adsorbate and adsorbent. This is called chemical adsorption. Forces such as different electrical charges try to keep adsorbate and adsorbent apart. Therefore, the adsorbate must have enough energy to overcome these forces. Chemical adsorption appears more often when high temperatures are present. Compared to physical adsorption, the bond between adsorbent and adsorbate is stronger when a molecule is chemically adsorbed, and more energy is released. Due to the strong bond, film diffusion is smaller when molecules are chemically adsorbed. Nevertheless, adsorption onto activated carbon is usually physical rather than chemical (Safa and Bhatti, 2011). In adsorption process, there are different types of adsorbents, but the most popular and commonly used is activated carbon. AC is very good for both gas-phase and liquid-phase purification. AC for gases purification through adsorption has played a major role in air pollution control. Adsorption of organic and dissolved materials from solution is another area where activated carbon has found major application. Adsorption is now major method used worldwide for water, wastewater and gases treatment to remove hazardous compounds to human and living organisms. Adsorption of contaminants from solution onto adsorbent may result from adsorbate hydrophobicity or from a high affinity the solute has for adsorbent. The contaminants removal from solution can either be by hydrophobicity or solute affinity for carbon factors during treatment process. Hydrophobicity is repelling or failing of a substance or material to mix with or dissolve in water. When a substance is soluble or dissolves in water, there is solubility compatibility between that substance and water. Hydrophobicity is the tendency of material to mix with or dissolve in water. The more hydrophilic a substance is, the less likely it is to be adsorbed. And a hydrophobic substance will more readily adsorbed. Also, when the solute has affinity for carbon, then that substance will be readily adsorbed by the carbon too.

2.18 Adsorption system

The adsorption process can be carried out using at least three adsorption system listed below:

- **a.** Batch contact system
- **b.** Fixed bed
- **c.** Pulsed bed

2.18.1 Batch contact

In batch process, wastewater is mixed with an amount of carbon and this mixture will be subjected to stirrer or agitation until the adsorptive (contaminants) have been reduced to a desired level. The filter paper is then used to separate carbon from filtrate. The carbon removed can either be regenerated for re-use or completely discarded. Regenerated carbon can be used for another volume of solution.

2.18.2 Pulsed bed

Adsorption can be carried out in a pulsed bed. Pulsed bed is an adsorption process where saturated carbon is removed at a constant time intervals from the bottom of the column and is replaced by fresh carbons. Any time carbon is removed, it is always kept for regeneration and this make pulsed bed to be advantageous for better utilization of activated carbon.

2.18.3 Fixed bed

Fixed bed has advantage over batch contact because adsorption rate depends on solute concentration in the mixture being treated. In fixed bed the adsorption is progressively and continuously in contact with a fresh solution. The concentration of solute in a mixture is progressively in contact with layer of carbons. And the carbon layers power to take up contaminants in a column decrease and changes very slowly. The effectiveness of activated carbons to remove solute decrease as the concentration of the solute in contact with specific amount of carbon proceeds with time. For fixed bed the wastewater or water to be purified and treated is passed through a stationary bed of activated carbon in a column. In fixed bed, adsorbents continue to pick up impurities from water or wastewater over the entire operation period. In this operation non-steady state condition set in. in fixed bed, the fresh few layers of carbon during the initial stages of operation effectively adsorbed the impurities. During the starting time of adsorption process, solution at its peak of solute concentration (C_o) is in contact with first layers of activated carbon. The adsorbents will pick up some solute layers from the solution, but some solute will escape the first layer of carbon and move to the next layer of carbon. The solutes that escape the first layer of activated carbon are then picked up from the solution in the few second layers and those that escape the second layer is then picked up in the subsequent strata or layers and at the end no solute escape from the adsorber. But observation shows that in this operation solute concentration in a solution is decreasing progressively through the layers of adsorbent beds in the column, and that the primary adsorption zone is at the first few layers of adsorbents. But as the contaminated or wastewater feed continue to enter and move down the column, the first layer of carbon become saturated with no or less capacity to remove solute at this stage, the primary adsorption zone move from the first few layer of the column to second few layers, and this zone becomes the zone where much solute is removed from feed water and the second few layers become the zone or region of fresher adsorbent. As the operation proceeds the wavelike movement will set in within the column and the primary adsorption zone will proceed from these initial first few layers of adsorbent and move through the column until the last or final few layers of adsorbent becomes the primary adsorption zone. And as the primary adsorption zone proceeds from the initial to the final layers of adsorbent, more and more solute will escape from the effluents due to the fact that the saturated layers become ineffective in adsorbing solute, and the solute moves down, the effective layer of carbon may not be too thick enough to remove the solute, while some solutes are removed, some will find their way out of the adsorbent bed and escape with effluent.

2.19 Adsorption equilibrium

Adsorption process operation requires varied mechanisms such as external mass transfer of adsorbate onto adsorbent which is followed by intra-particle diffusion. Adsorption equilibrium is activated when the rate at which molecule desorbs is equal to the rate at which molecule adsorb onto the surfaces. The theory is being proposed to explain the physical chemistry involved in adsorption, but this physical chemistry is of no or little importance to engineers, engineer only require data at equilibrium conditions. Literature also revealed that most of the theory developed for adsorption system is developed for gas-solid system (Jain *et al*., 2009). Until now theory developed for liquid–solid systems is difficult to understand, so gas solid system is commonly used for liquid-solid system. The most commonly used equilibrium models for adsorption system calculation and understanding are Temkin, Frumkin and Langmuir isotherm. Adsorption is a process where solutes are removed from solution and their concentration at the surface, until equilibrium is reached between the amount of adsorbate remaining in solution and that at the surface. When we express the amount of solute adsorbed per unit weight of adsorbent qe as a function of concentration C of adsorbate remaining in solution, this is the equilibrium of adsorption, which can be called an adsorption isotherm. For wastewater and water applications, the two equations that fit for adsorption description are Freundlich and Langmuir equations. The adsorption isotherms are important for describing the functional dependence of capacity on pollutant concentration and for representing the capacity of adsorbents for the removal of organics from wastewater. The effectiveness of activated carbon can be determined by how steeper the isotherm for determining the feasibility of adsorption for treatment, for carbon dosage requirement estimation and for carbon per size selection, then experimental determination of the isotherm is routine activities required in evaluating all these written above. Experimentally observed dependence of capacity on concentration, equilibrium condition relates to the adsorption isotherm. In most adsorption process, the practical time of detention for treatment application is not always sufficient for true equilibrium to be obtained. For more rapid approach to equilibrium, rate of adsorption are very significant for knowing the fraction of equilibrium capacity used in a given system. The interaction of adsorbates with adsorbent can be described by the adsorption isotherms. It is also important in adsorbent optimization. For adsorption data prediction and interpretation, the correlation of equilibrium data using either empirical or a theoretical equation is very necessary. The Freundlich and Langmuir equations can be used as mathematical description experimentally; the four common isotherms are Temkin, Sips, Langmuir and Freundlich isotherm. The significance of the adsorption is gotten by correlation coefficient (R^2).

2.19.1 Freundlich isotherm

The German physical chemist, Herbert Freundlich a model that can be used in adsorption process called Freundlich model. Many models are available to describe the adsorbate/adsorbent system. The Langmuir and the Freundlich model are the most often used. The latter is particularly good if the concentration of the compound in the liquid is very low. Therefore, it is usually preferred over the Langmuir isotherm. The Freundlich model is described by the relationship

$q = K_F C_e^{1/n}$ (2.3)

Where K_F and $1/n$ are Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, while qe is the colour adsorbed per unit weight of adsorbent (carbon).The amount of solute adsorbed and concentration of solute in solution can be represented by qe and Ce respectively. Equation (2.3) can be linearized to the form shown in Equation (2.4), and the constants can thus be determined numerically.

$\text{Log } q_e = \log K_f + \frac{1}{n}\log C_e$ (2.4)

A plot of log q_e versus log C_e is a straight line with the interception at y-axis representing the value of log K_F with slope $\frac{1}{n}$. The linear plot showed the applicability of Freundlich isotherm to both adsorbents. The value of $\frac{1}{n}$ which is closer to 0 means the adsorption is more heterogeneous. A value for $1/n$ below one indicates a normal Freundlich isotherm while $1/n$ above one is an indicative of cooperative adsorption or ($1/n = 0$), favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$).

The capacity constant k and the intensity constant 1/n are parameters related to the system of adsorbent and adsorbate (Jain, Garg and Kadirvelu, 2009). In order to determine the parameters K and 1/n, isotherm experiments need to be conducted. An aqueous solution containing a defined mass of the desired compound and a defined mass of activated carbon is mixed in a flask for batch adsorption. Samples are taken after defined time periods. Adsorption equilibrium occurs when the concentrations of the compound in the solution and on the carbon are stable. The amount of adsorbate can be calculated from the concentration difference in the solution at the beginning and the end of the experiment, multiplied by the volume of liquid. Each experiment defines one point in the isotherm. The next point can be determined by adding a defined mass of the same adsorbate to the system and repeating the same procedure. Another way to determine several points of the isotherm is using individual flasks for several compound concentrations or liquid volumes. The parameters K and 1/n can be calculated using the Freundlich model.

2.19.2 Langmuir isotherm

The Langmuir isotherm was evaluated using the model

$$\frac{C_e}{q_e} = \frac{1}{Q_L \ K_L} + \frac{C_e}{Q_L} \tag{2.5}$$

Where C_e is the equilibrium concentration (mg/ L), q_e is the amount adsorbed at equilibrium (mg/ g), while, Q_L (mg/ g), and K_L (L/ mg) are Langmuir constants. Q_L is capacity of adsorption and K_L is adsorption energy. The linear plots of Ce/qe against Ce, reveals which isotherm model is obeyed by the adsorbents. The values of Q_L and K_L will be determined for all adsorbents from intercept and slopes of the linear plots. The shape of the Langmuir isotherm will be investigated by the dimensionless constant separation term (R_L). R_L is being calculated as follows:

$$R_L = \frac{1}{1 + K_L \ C_0} \tag{2.6}$$

R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) and unfavorable ($R_L > 1$) (Jain *et al.*, 2009). To determine the adsorption feasibility for a particular selected carbon for adsorption process, then experimental determination of the isotherm is important. This will help in determine the carbon pore volume and carbon requirement to carry out effective and efficient adsorption process. Freundlich and Langmuir are useful for mathematical description of the experimentally observed dependence of capacity on concentration. The equilibrium conditions is related to adsorption isotherm, however, most treatment applications do not provide enough detention time and sufficient time for equilibrium to be attained or obtained $R_{L.}$

2.20 Experimental design

Designed experiments require some up front planning to be successful. Before the right design can be chosen for a product or a process, a number of things will need to be decided. This may include

- Objectives of the design
- Responses to be measured and how to measure them
- Factors to be studied and at how many levels
- Number of runs to be made that will provide enough power to estimate the effects of the choosing factors on the process or the products.

The major objective of experimental design is to identify the significant factors and to screen out insignificant factors. When the objective is set on the idea of how the factors are interacting and how the interaction of the factors are affecting the process or the product, the possible design to set to achieve this objective is factorial design (Lee *et al*., 2012). Response surface design can be used to characterize how the significant factors affect the responses. It can also be used for optimization purposes. So to study factors at 3-levels, Box – Behnken is applicable. To study factors at 5-levels, central composite is applicable. D-optimal will create a custom design based on the type of polynomial that must be fit in to design. Factorial design is good so study factors at 2-levels.

2.20.1 Factorial design

Factorial designs are used primary for screening significant factors, but can also be used sequentially to model and refine a process. In the design expert software, a number of factorial design types can be chosen. Some of the factorial design types include 2-level factorial design, Min Res V designs, Min Res IV designs, Irregular fraction designs, General factorial designs, D-optimal designs, Plackett-Burman designs and Taguchi designs. All these factorial designs – are tools that allow one to experiment on many factors simultaneously (Safa and Bhatti, 2011)

2.20. 2 Two – level factorial designs

The 2-level factorial design builder dialog box offers two-level full factorial and fractional factorial designs. It can be used to investigate 2 to 21 factors using 4 to 512 runs. This collections of designs provides an effective means for screening through many factors to find the critical few. 2-level factorial designs permit the estimation of all main effects and all interaction effects. Design-Experts offer a wide variety of fractional factorial designs and will also calculate detail information on the alias structure, which must be inspect or observe to be sure that the selected design estimates the interactions of interests. Many different effects tool exist that can be used to study the main and interaction effects of design factors. Some of these tools include Half-Normal Plot, Normal Plot. Pareto Chart, Effects List, ANOVA etc.

2.20.3 Factor coding in factorial design

Design descriptions and analyses for designed experiments are best done with coded factors. Coding reduces the range of each factors to a common scale. Generally, - 1 to + 1, regardless of its relative magnitude. Also, it may be easier to think in term of changes from low to high for the factors than to think about their actual values, especially when thinking about squared terms and interactions. For example, one factor may vary from 0.1 to 0.5 while another vary from 200 to 800. Typical coding has -1 as the lower level of a factor, +1 as the upper level, and 0 as the middle level. The value used for coding are called contrasts.

2.20.4 Factorial model

A factorial model is composed of a list of coefficients multiplied by associated factor level. That model is in the form of

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{123} ABC \qquad (2.7)$$

Where: Y is the predicted response (removal efficiency %), β_0 represents the intercept, β_n is the coefficient associated with factors, n. The letters A, B and C represents the factors in the model. Combination of factors such as AB, BC and AC represent an interactions between the individual main factors in the term. From the equation above, we have order and description as follow:

Table 2.1: Factorial Model Order and Descriptions

	Order
Zero	Intercept
First	Main effects: A, B and C
Second	2-factors interactions(2FI): AB, AC and BC
Third	3-factors interactions(3FI): ABC

2.20.5 Factorial design analysis process

After the response data are entered into design layout view, response is choosing by clicking on the corresponding node under analysis on design expert software. The displaced information must be followed in sequential order to analysis the response. The sequential order include transformation, effects plot, model etc.

2.20.5.1 Response transformation

Transformation of the response is an important component of any data analysis. Transformation is needed if the error (residual) is a function of the magnitude of the response (predicted values). The available transformation on the design expert include, square roots. Natural log, base 10 log, inverse square root, power, logit etc. The appropriate transformation choice relies on subject matter or statistical consideration.

2.20.5.2 Factorial effects

Factorial effects tools include:

- **Half-Normal plot and Normal plot:** probability plot can be used to choose significant effects. From the plot, the Shapiro-Wilk test for normality should have a high p-value (above 0.10) to indicate that there is no deviation from the assumption of normality for the non-selected points.
- **Effects list:** any factor selected from either half-normal or normal plot will also be shown as selected on the effects list and vice-versa

- **Pareto chart:** this is additional graphic tool used to display the t-value of the effects. Though half-normal plot of effects is normally used to choose the statistically significant effects, but Pareto chart is clearer and comfortable to view those effects that are significant in a bar chart form. There are two different t-values plotted on the graph – based on the Bonferroni corrected t and standard t. these t-limits are only approximate to the 5% risk level. From the Pareto bar chart, effects that are above the Bonferroni limit are almost certainly significant. Effects that are above t-value limit are possibly significant and should be added to the model. Effects that are below the t-values limit are not likely to be significant.
- **Analysis of variance (ANOVA):** ANOVA helps to confirm that only statistically significant effects are analyzed in the chosen model.
- **Diagnostics:** This tool evaluates model fit and transformation choice with graph.
- **Model Graph:** This is used to interpret and evaluate the model.

All these tools are useful in the identification of significant effects, insignificant effects and effects interactions.

2.21 Raman spectroscopy

Raman spectroscopy is the formation and study of Raman scattering for the purpose of identifying molecules. Raman scattering is formed by X-raying a sample with a light source at one precise color and wavelength. The light source for irradiating a sample is usually in the form of a laser. For Raman to work in identifying a sample molecules, the laser has to be at a wavelength that molecule of the sample cannot absorbed. Raman spectroscopy has been an important tool that is particular sensitive to the microstructure of the carbon. Raman spectrum, thus providing useful diagnostics for carbon structure and properties. Many research works were based on information about the physical basis of the observed Raman spectra, with particular emphasis on relationships of Raman spectra with carbon microstructure. Raman spectroscopy is one the method that can be used to characterize carbon materials. Raman is a useful and valuable method that can be of great advantage to carbon material characterization. Raman is very well suitable to detect small changes in structural morphology of carbon materials, this is making it an essential instrument for many material scientists working with carbon structures (Ferraro *et al*., 1994).

CHAPTER THREE

3.0 RESEARCH METHODOLOGY

3.1 Materials and chemicals used

Table 3.1: List of materials and chemical used

S/No	Material and Chemical	Source
1	**Methylene blue**	**Panlac, Minna**
2	**Brilliant green**	**Panlac, Minna**
3	**Distilled water**	**WAFT lab, FUT**
4	**Modified and unmodified carbons**	**WAFT lab, FUT**
5	**HCl and NaOH**	**Chemical lab**
6	**Sample bottles**	**Panlac, Minna**
7	**Glass wool**	**Panlac, Minna**
8	**Filter paper**	**Panlac, Minna**
9	**Funnel**	**Panlac, Minna**
10	**White 2 liter kegs**	**Panlac, Minna**

3.2 Equipment used for experiments

Table 3.2: List of Equipment Used

S/No	Equipment	Manufacturer
1	Retort stand	
2	Ultra-violet spectrophotometer	UV – 1800 Shimadzu, China
3	pH meter	
	Weighing balance	
4	Beakers	
5	Thermometer	Cyberlab, USA
6	Water bath with shaker	Pyrex, England
	Glass column	
7	Conical flasks	Daihan Labtech, Korea
8	Drip bag	Pyrex, England
	Measuring cylinder	
9	Oven	CG17, England

10	Muffle hotspot furnace	Dana house, Minna
11	Crucible	Pyrex, England
12	Muslin cloth	Genelabwides, England
13		Genelabwides, England
14		Gallemkamp, England
15		Gallemkamp , England

3.3 Characterization of adsorbent by Raman spectroscopy

For adsorbents characterization by Raman Spectroscopy, Raman signal was collected by a detector and a computer creates a graph showing the intensity of light at each wavenumber. The change in energy was observed in terms of "Raman shift" with respect to excitation frequency of the incident beam, while the magnitude of the shift itself is independent of the excitation frequency. This Raman shift is, therefore, an intrinsic property of the sample. In general, only some excitations of a given sample were "Raman active," that is, only some take part in the Raman scattering process. The peaks in the intensity occur at the frequencies of the Raman active modes. Using selection rules that govern the ability of a molecule to be detected using Raman spectroscopy. Each molecular bond is characterized by unique energy transitions and subsequent shifts in wavelength of the original beam (Raman shift). Measuring the wavelength shift allows the identification of molecular species on the sample surface. Therefore, Raman spectroscopy provides details on the chemical composition and molecular structure of carbon samples. Raman spectra "fingerprints" for all characterized carbons provides information of the molecular structure of the carbon samples used for this experiments.

3.4 Brunauer-Emmet-Teller (BET)

BET method is used for the determination of the surface area of most porous materials. Total surface area is a crucial parameter since it helps to known the accessibility of the active site of probing molecules. Surface area of modified and unmodified kaolin are carried out by nitrogen adsorption which is generally known to refer to the enrichment of one or more of a component between two bulk (gas and liquid) which is the adsorbate. Nitrogen is usually the preferred adsorptive material because of quadra-pole moment that is permanent and it is responsible for the formation of well-defined monolayer on most surfaces.

3.5 Sources of raw materials

The precursors used in the production of the adsorbents include coconut shells, flamboyant pod, eucalyptus tree and corn cob. Coconut shells were obtained from local market in Minna (Niger state). Flamboyant pod was sourced within Federal University of Technology main campus, Gidan-kano, Minna. Corn cob was bought at Kasanguari village, Minna Territory. Eucalyptus tree was sourced for on the farm land located in Minna Territory. The precursors were sorted to remove stones, and debris, thereafter each agricultural waste was kept separately for further treatment. Coconut shells, flamboyant pod, eucalyptus tree and corn cob obtained were then washed with tap water, to remove surface impurities, and were air – dried in sunlight. They were then stored in dry containers prior to carbonization

3.6 Carbonization

1 kg of each agricultural waste material was charged into the electric muffle furnace which was then heated by in the absence of oxygen at a temperature of 600^{o}C for one hours. The resulting charred material was collected and cooled at room temperature.

3.7 Activation

Samples of the carbonized material were weighed on electric weigh machine, soaked in one mole of phosphoric acid (H_3PO_4) 63 % concentrated solution for 24 hours (Jain *et al*., 2009). The materials were then removed from the soaking after 24 hour lapsed and then washed with distilled water until leachable impurities due to free acid and adherent powder were removed and the pH of the water was 7. Finally, the samples were drained and dried in an oven at 110°C 12 hours.

3.8 Preparation of dye solution (Adsorbate)

The accurately weighted (0.003 gram) of each methylene blue and brilliant green were dissolved in a distilled water to prepare dye mixture stock solution. 1000mg/L stock solution of synthetic waste water was prepared using blue and green dye and from which other desired concentrations were obtained. The pH of the working solutions was adjusted to the required values of 4 and 11 by adding 0.1 M HCl or NaOH.

3.9 Batch studies

Batch adsorption experiments were carried out at ambient temperature (26^{0}C). The experiments were run in 250ml conical flasks using water bath with shaker at 130rpm. Three parameters were interchanging at each run for total of eight batch experiments.

3.9.1 Factorial matrix for batch experiments

To systematically explore process options, a full-factorial two-level design on the key factors was set up. Only three factors of all the factors affecting dye adsorption efficiency were studied in this work. The three factors are contact time, dosage and pH. The symbols of minus (-) and plus (+) were used to designate low and high levels, respectively.

Table 3.3: Test Factors for Dye Adsorption.

Factor	Name	Units	Low level (-)	High level (+)
A	Contact time	Minutes	30	90
B	Dosage	Gram	2	5

At each C pH 4 11

combination of these process settings, the adsorption rate was recorded. The goal is to maximize the adsorption rate and also to try to find conditions that allow a reduction in the concentration of dye in solution and increase dye removal efficiency. Two responses were considered for the experiment on dye adsorption: MB removal and BG removal. Both the MB and BG removal in percent were calculated using the formulae:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \qquad (3.1)$$

Where, C_i is the initial colour concentration and C_f final colour concentration. Table 3.4 shows the matrix used for the batch experiments carried out using factorial method

Table 3.4 Batch experiment factorial design template

Number of runs	**A**	**B**	**C**	**Time (mins)**	**Dosage (g)**	**pH**
1	_	_	_	30	2	4
2	+	_	_	90	2	4
3	_	+	_	30	5	4
4	+	+	_	90	5	4
5	_	_	+	30	2	11
6	+	_	+	90	2	11
7	_	+	+	30	5	11
8	+	+	+	90	5	11

Plate I: Water Bath with Shaker

3.9.2 Effect of contact time

The agitated time of adsorbents with adsorbates was varied for all the experiments run between 30 minutes and 90 minutes for both raw and activated carbons experiments. 8 set of experiments were run using 2^3 factorial design template. At the end of each set of experiment, the supernatant solutions were taken to the laboratory for absorbance analysis. The shaker speed of 130rpm was kept constant throughout the experiments run

3.9.3 Effect of adsorbent dosage

The adsorbent (raw and activated) was varied for all the experiments run between 2g and 5g. 8 set of experiments were run using 2^3 factorial design template. At the end of each set of experiment, the supernatant solutions were taken to the laboratory for absorbance analysis. The shaker speed of 130rpm was kept constant throughout the experiments run.

3.9.4 Effect of pH of the adsorbate

The pH was varied for all the experiments run between 4 and 11. The pH of each solution was adjusted with 1M HCl or 1M NaOH before the adsorbent was mixed. The shaker speed of 130rpm was kept constant throughout the experiments run. After the completion of each experiment, the conical flask was withdrawn from the shaker at the predetermined time interval and the supernatant solution was separated by filtration using whatman filter paper. The final concentration of MB and BG was then analyzed for absorbance by using Ultra-violet spectrophotometer at 664nm and 629nm along with a blank solution as control.

Experimental diagrams

Plate II: Precursor carbonization process

Plate III: Dye stock solution

Plate IV: Adsorbent inside containers

3.10 Column studies

Column studies were carried out in a glass column of a known diameter and height. Glass wool was used in packing the adsorbent at both end of the glass. A known concentration of synthetic waste water of dyes was passed in through a drip bag connected to a flow set (valve) used in the adjustment to the desired flow rate. Samples were then collected at predetermined time interval for analysis by using U-v spectrophotometer. Conditions of the experiments are as follows: Column adsorption experiments were carried out at ambient temperature (26^0 C).

Plate V: Experimental set up for column adsorption studies

3.10.1 Effect of flow rate

The flow rate of dye solution through adsorbents mass was varied for all the experiments run between 4.3 mL/min. and 8.6 mL/min. After the completion of each experiment and Prior to each experiment, distilled water was passed through the column to rid the column impurities and air bubbles. The final concentrations collected at interval were then analyzed for absorbance by using Ultra-violet spectrophotometer at 659nm and 626nm along with a blank solution as control.

3.10.2 Effect of adsorbent mass

The adsorbents mass was varied for all the experiments run between 10.6g and 15.9g. After the completion of each experiment and Prior to each experiment, distilled water was passed through the column to rid the column impurities and air bubbles. The final concentrations collected at interval were then analyzed for absorbance by using Ultra-violet spectrophotometer at 659nm and 626nm along with a blank solution as control.

3.10.3 Effect of pH of the adsorbate

The pH was varied for all the experiments run between 4 and 11. The pH of the solution was adjusted with 1M HCl or 1M NaOH. After the completion of each experiment and Prior to each experiment, distilled water was passed through the column to rid the column impurities and air bubbles. The final concentration of MB and BG was then analyzed for absorbance by using Ultra-violet spectrophotometer at 664nm and 629nm along with a blank solution as control. The percentage colour removal was then calculated using equation (3.1). The uptake of dye at equilibrium time was calculated from:

$$q_e = \frac{(C_0 - C_e)v}{1000w} \times 100 \qquad (3.2)$$

Where q_e is the amount of adsorbed dye in mg/g. C_o and C_e are the initial and equilibrium dye concentration in mg/L, V is the volume of the aqueous solution in ml and W is the mass of the adsorbent in g.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Raman spectroscopy graphs

By direct comparison of these spectra of the unknown compounds with catalogue of known compounds, this work permit qualitative analysis of individual compounds in each of the carbon used for the experiments.

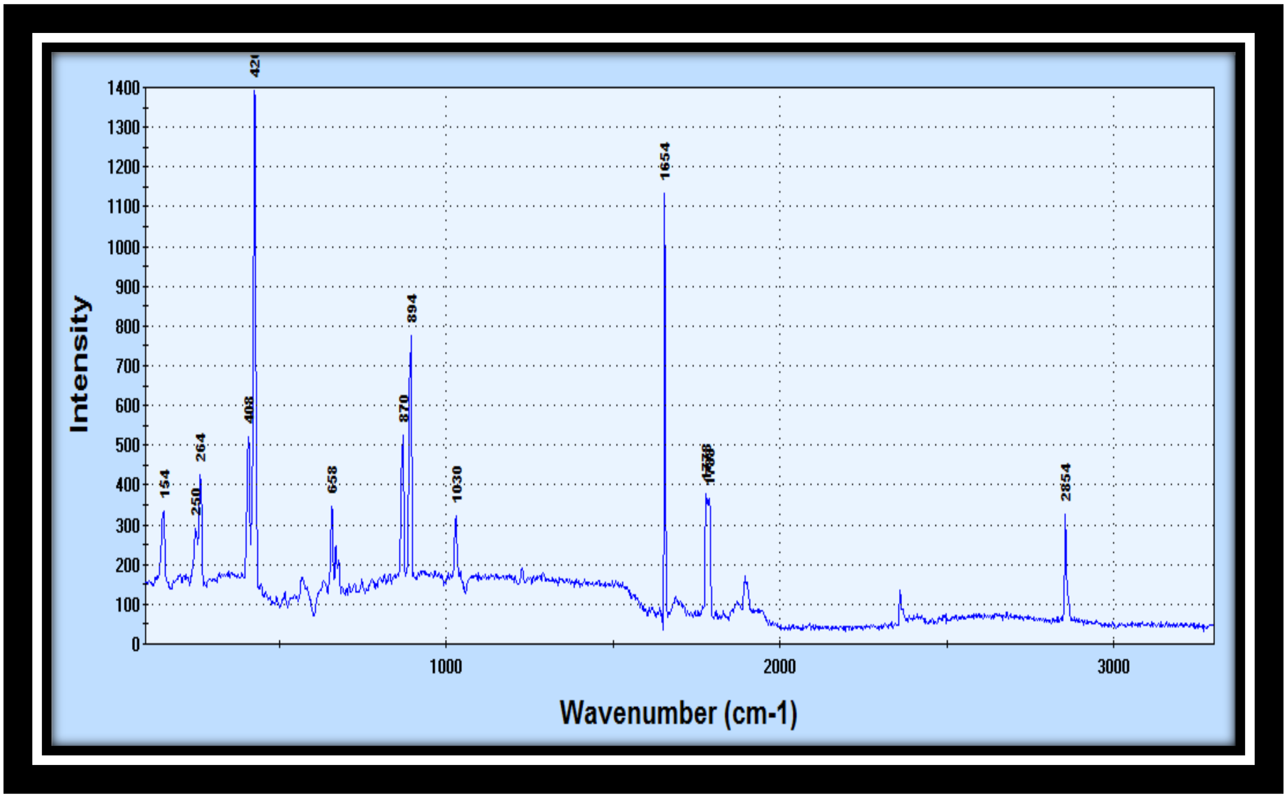

Figure 4.1: Coconut shell PAC

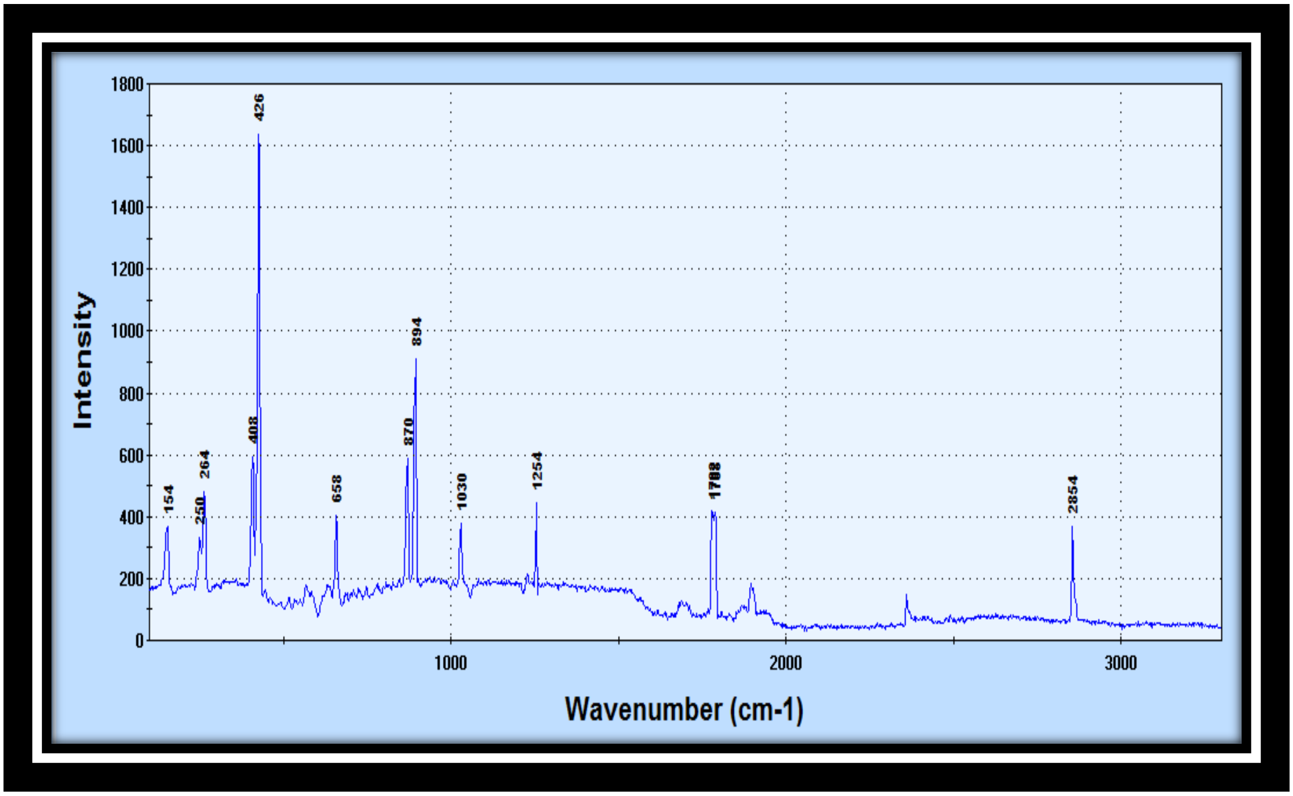

Figure 4.2: Coconut shell GAC

When the peaks from Figures 4.1 and 4.2 were compared with Joseph *et al.* (1987) catalogue of known compounds, it was possible to recognize bands at specific positions which was identified as "characteristic group frequencies" associated with the presence of a particular molecular structure. The peak centered at 154 and 264cm^{-1} is associated with CC aliphatic chain. The peak centered at 408 and 428cm^{-1} is associated with alkane functional group (- CH_2 -) that is, methyl. The peak at 658cm^{-1} is associated with sulphur groups ($CH_2 – S – CH_2$). The peak centered at 870 and 894cm^{-1} is associated with carbonyl compound (C – O). The peak at 1030cm^{-1} is associated with aliphatic fluoro compounds (N – F). The peak at 1654cm^{-1} and 1786cm^{-1} is associated with benzophenones compounds (C = O). The peak at 2854cm^{-1} is associated with primary amides (N – H). The peak at 2976cm^{-1} is associated with (O – H) phenol (Joseph *et al*., 1987). The peaks from the graphs in Figures 4.1 and 4.2 provide information on physical characteristics such as functional group, crystalline phase and orientation, polymorphic forms, and intrinsic stress of the carbons used in this work.

4.2 BET analysis

Brunauer-Emmet-Teller (BET) analysis results are shown in Table 4.1. Adsorption capacity is the most essential property of activated carbon (Guo and Lua, 2002) which is relative to the BET surface area. Thus, from the results obtained for uptake of MB and BG, activated carbon has more adsorption capacity than unactivated carbon, this is due to larger surface area in activated carbon when compares to smaller surface area in unactivated carbon. The trend of these results follows that of Guo and Lua, (2002).

Table 4.1: BET analysis results for coconut shell carbons

Sample	BET surface area (m^2/g)	Pore volume (cm^2/g)	Pore size (Å)
Unmodified carbon	145.4927	0.09426	24.2145
modified carbon	270.9518	0.148872	18.9372

4.3 Adsorption experimental results

4.3.1 Results obtained for methylene blue adsorption

Presented in Table 4.2 are the results obtained for methylene blue dyes adsorption during batch experiments.

Table 4.2: MB Adsorption by coconut shell

Number of runs	Final conc. using activated carbon	% removal by activated carbon	Final conc. using raw carbon	% removal by raw carbon
1	0.000750	75.0	0.001023	65.9
2	0.000450	85.0	0.000858	71.4
3	0.000600	80.0	0.001035	65.5
4	0.000300	90.0	0.000795	73.5
5	0.000600	80.0	0.000093	69.0
6	0.000540	82.0	0.000834	72.2
7	0.000240	92.0	0.000780	74.0
8	0.000150	95.0	0.000768	74.4

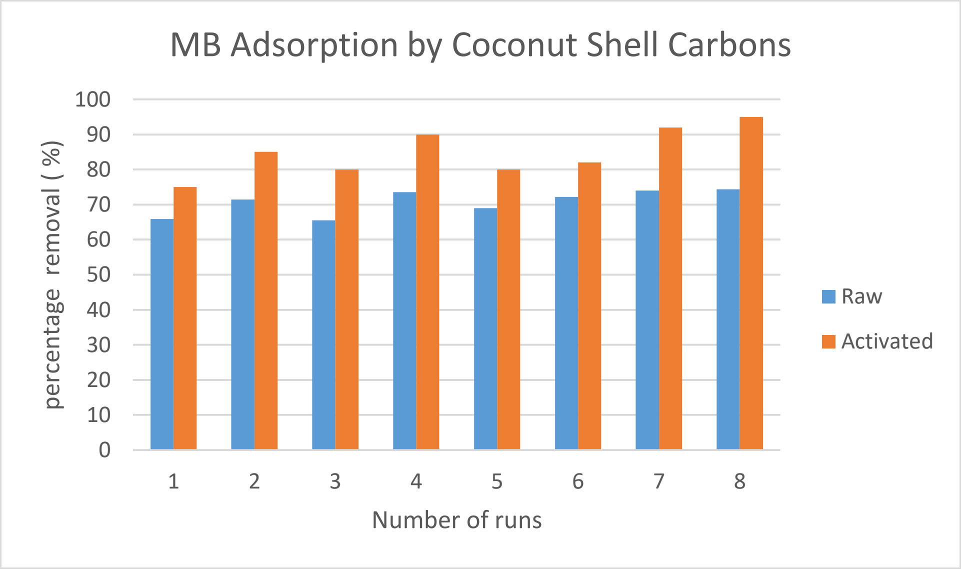

Figure 4.3: Adsorption by raw and activated carbons

4.3.2 Results obtained for brilliant green adsorption

Presented in Table 4.3 are the results obtained for brilliant green dyes adsorption during batch experiments.

Table 4.3: BG Adsorption by coconut shell

Number of runs	Final conc. using activated carbon	% removal by activated carbon	Final conc. using raw carbon	% removal by raw carbon
1	0.000750	75.0	0.001089	63.7
2	0.000510	83.0	0.000888	70.4
3	0.000630	79.0	0.001428	52.4
4	0.000300	90.0	0.000798	73.4
5	0.000570	81.0	0.000927	69.1
6	0.000510	83.0	0.001134	62.2
7	0.000180	94.0	0.000867	71.1
8	0.000090	97.0	0.000756	74.8

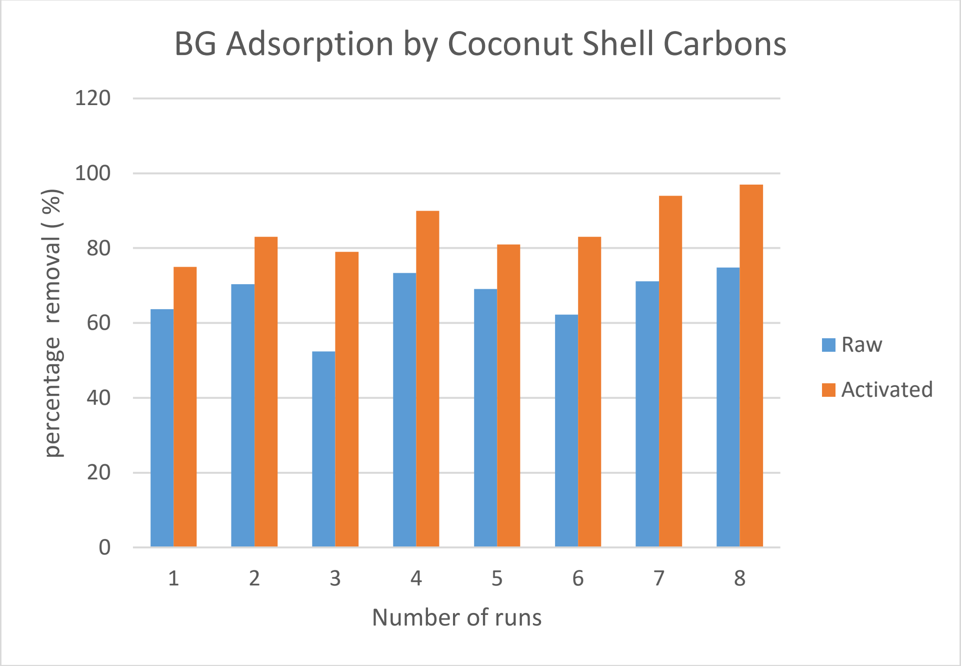

Figure 4.4: Adsorption by raw and activated carbons

The Figures 4.3 and 4.4 show the comparison of the dye adsorption during batch experiments using activated and un-activated carbon. The graphs clearly show that the activated carbon adsorption capacity is higher during adsorption process than un-activated carbon. All the activated carbons used during the experiments adsorbed dye from the dye solution more than all the un-activated carbons used for the experiments. The percentage removal of all activated carbons is higher than all the un-activated carbons percentage removal. From the data generated during the experiments in Tables 4.2 and 4.3, the graphs were plotted using the percentage removal in each experiment against number of runs for both activated and un-activated carbons. Also, the tables 1, 2, 3, 4, 5 and 6 in appendix B revealed that flamboyant pod activated carbon, corn cob activated carbon have the highest adsorption capacity for MB and BG than coconut shell activated carbon and eucalyptus activated carbon. And the overall results revealed that flamboyant pod activated carbon removed dyes from wastewater than all the other activated carbons used for the experiments. The decreasing order of removal capacity is flamboyant pod, corn cob, coconut shell and eucalyptus tree. All the carbons except flamboyant pod were activated using the same conditions of carbonization of 500^0C for 1 hour and activation was done with 1 mole of 63% phosphoric acid and soaked for 24 hours. Flamboyant pod carbonization temperature was at 500^0C for 15minutes and activation was also done with 1 mole of 63% phosphoric acid and soaked for 24 hours just like others. At carbonization of 1 hour at 500^0 C, the flamboyant pod turned to ash.

4.4 Two-level factorial design

4.4.1 MB and BG adsorption factors and interactions

The results from running all combinations of the chosen factors, each at two levels, are shown in the Table 4.4. MB adsorption ranged from 75 to 95 percent and BG adsorption ranged from 75 to 97 percent.

Table 4.4: Results from batch adsorption experiment

Standard Order	Run Order	Factor 1 A: Contact Time (minutes)	Factor 2 B: Dosage (gram)	Factor 3 C: pH	Response 1 MB adsorption (percent)	Response 2 BG adsorption (percent)
1	1	-30	-2	-4	75	75
2	2	+90	-2	-4	85	83
4	3	-30	+5	-4	90	90

7	4	+90	+5	-4	92	94
6	5	-30	-2	+11	82	83
5	6	+90	-2	+11	80	81
8	7	-30	+5	+11	95	97
3	8	+90	+5	+11	80	79

The run order of this experiment was randomized to offset any lurking or putting off variables. By randomizing the order of this experiments, the chance of running all low levels of a factor and then all high levels of a given factors was greatly reduced. The first column in Table 4.4 lists the standard order on which laboratory experiments were carried out. The mathematical symbols of minus and plus, called "coded factor levels" were placed next to the "actual levels" at their lows and highs, respectively. The run numbers were selected from a table of random numbers and these numbers were mark on slips of paper and affixed to the conical flask used for the experimentation.

4.4.2 Orthogonal arrays

The standard two-level factorial layout shown in Table 4.4 is one example of a carefully balanced "orthogonal array". Technically, this means that there are no correlation among the factors. By observation of column C, we can see this clearly. When C is at the minus level, factors A and B contain an equal number of pluses and minuses; thus their effect cancels. The same results occurs when C is at the plus level. Therefore, the effect of C is not influenced by factors A and B. the same can be said for the effects of A and B and all the interactions as well. Any orthogonal test array is much better than unplanned experimentation (an oxymoron). Happenstance data is likely to be highly correlated (non-orthogonal) and this makes it much difficult to sort out the factors that really affect the response.

4.4.3 Main and interaction effects

This analysis began by investigating the “the main effects” on the first response, MB adsorption. The focus was on factor A (contact time) first. Mathematically, the calculation of an effect is expressed as follows:

$$Effects = \frac{\sum Y+}{n+} - \frac{\sum Y-}{n-} \qquad (4.1)$$

Where “n” is refer to the number of data points collected at each level.

Y+ refers to all the run where factor A is at plus level (high)

Y- refers to all the run where factor B is at minus level (low)

The main and interaction effects calculated from the equation (4.1) is at the appendix A.

Table 4.5: Complete matrix of main and interaction effects calculated.

Standard	**A**	**B**	**C**	**AB**	**AC**	**BC**	**ABC**	**Response MB adsorption**	**Response BG adsorption**
1	_	_	_	+	+	+	_	75	75
2	+	_	_	_	_	+	+	85	83

3	_	+	_	_	+	_	+	80	79
4	+	+	_	+	_	_	_	90	90
5	_	_	+	+	_	_	+	80	81
6	+	_	+	_	+	_	_	82	83
7	_	+	+	_	_	+	_	92	94
8	+	+	+	+	+	+	+	95	97
Effects	-1.25	8.75	-1.25	0.25	-1.25	3.75	0.25	84.88	
Effects	6.0	9.5	7.0	1.0	-3.5	4.0	-0.5		85.25

The pattern of pluses and minuses for interaction effects is calculated by multiplying the parent terms. The AB column is the product of columns A and B, so for the first standard row, the combination of –A times –B produces +AB. The interaction effects were calculated by multiplying the parent terms. From the general formula shown previously, the main and interaction effects results are shown on the bottom line of the Table 4.4 above. For MB adsorption, from the Table 4.5, factor A, factor C and the combination of factor A and factor C produces negative effect or impact on MB adsorption. With that as a clue, a more closely look at the response 1 (MB adsorption), one will notice small adsorption of MB when both factor A and factor C are at their low levels. On an absolute value scale, the other interaction effects range from positive 0.25 (for AB) to as high as positive 8.75 (for B). Similarly, for BG adsorption, from the table above, factor A, factor C and the combination of factor A and factor C produces negative effect or impact on BG adsorption. With that as a clue, a more closely look at the response 2 (BG adsorption), one will notice small adsorption of BG when both factor A and factor C are at their low levels. On an absolute value scale, the other interaction effects range from positive 1.0 (for AB) to as high as positive 9.5 (for B). Could these just be chance occurrence due to normal variations in MB adsorption? To answer this question, let look at the normal plot, then we can see whether some or all of these effects vary normally.

4.4.4 Analysis of the results for MB adsorption.

4.4.4.1 Half normal plot for effects

Before plotting the effects, it helps to convert them to absolute values, a more sensitive scale for detection of significant outcomes. The absolute value scale is accommodated via a variety of normal paper called the “half – normal,” which is literally based on the positive half of the full normal curve. The vertical (Y) axis of the half-normal plot displays the cumulative probability while the absolute values of the effects on the x-axis.

4.4.4.2 Choosing effects to model

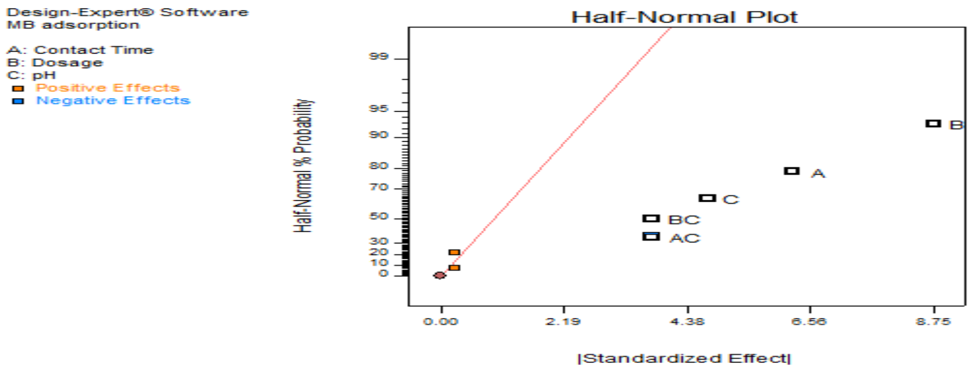

Figure 4.5: Half-normal plot of effects for MB adsorption.

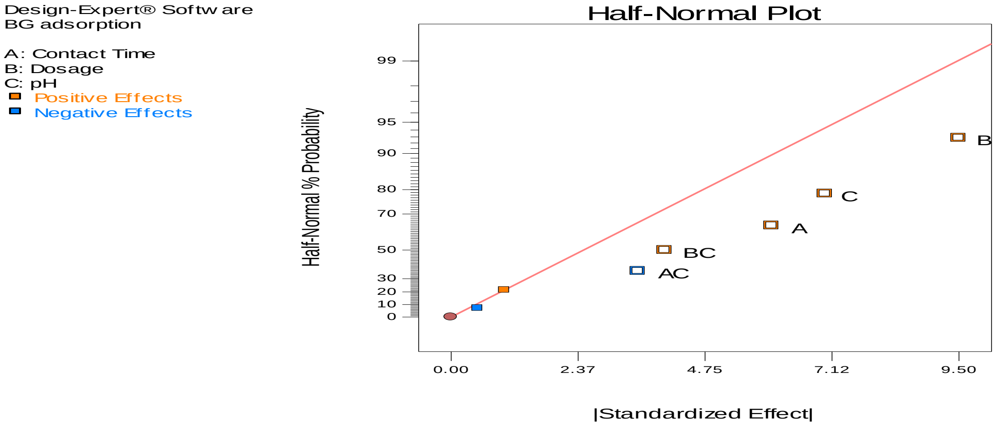

Figure 4.6: Half-normal plot of effects for BG adsorption

From the Figures 4.5 and 4.6, the biggest five effects fall well out on the tail of the normal curve (to the right). These five effects (A, B, C, AC, and BC) are most likely significant in a statistical sense. In other word, we need to focus on factors A, B, and C and how they interact as AC and BC to affect the response MB adsorption. To draw attention to these big effects, so we labeled them. When we observe the large gap before we get to the next lowest effect. From this point on, the effects (AB and ABC – from biggest to smallest, respectively) fall in line, which represents the normal scatter. The effects AB and ABC are left unlabeled to downplay their importance because they are insignificant. These two trivial and unimportant (insignificant) effects (nearest 0) will be used as an estimate of error analysis of variance (ANOVA). The pattern in Figures 4.5 and 4.6 is very typical: the two of the points fall in a line emanating from the origin, followed by a gap, and then one or more points fall off to the right of the line. The half-normal plot of effects makes easy to see at glance what, if anything, is significant.

4.4.4.3 Pareto chart of the effects

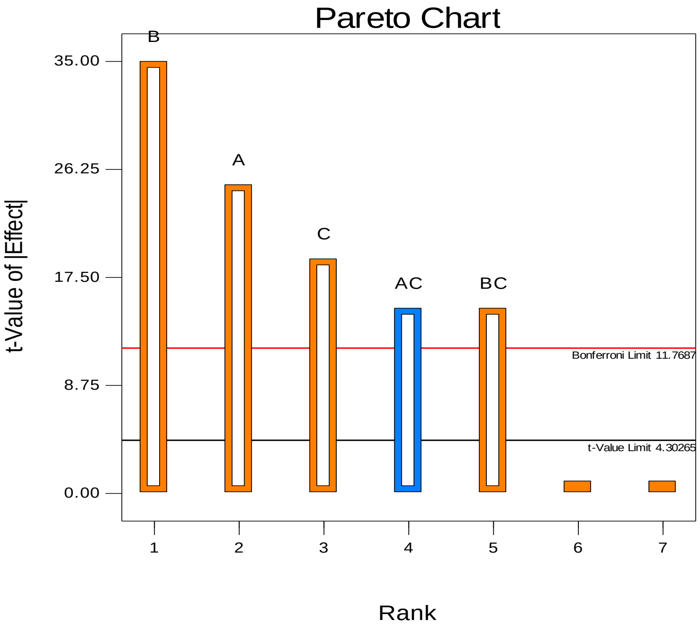

Figure 4.7: Pareto chart of effects for MB adsorption

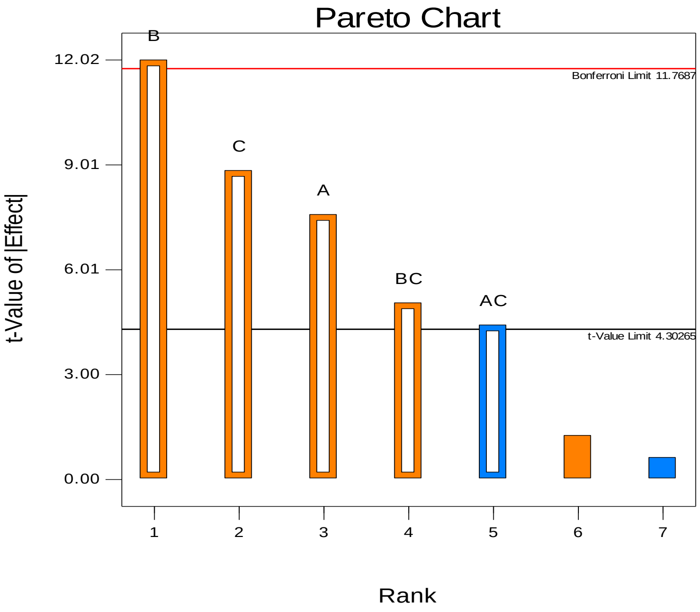

Figure 4.8: Pareto chart of the effects for BG adsorption

Pareto chart is plotted by performing calculations to obtain t-values each effect and for all the 7 effects, which were then bar charted in descending order. Before Pareto chart was plotted, two-tailed t-value for 0.05 probability which is the established threshold risk that can be accepted for significant of the effects was established. Also a more conservative t-value, named after its inventor (Bonferroni) can also be used to check for significance of effects. Both Bonferroni and t-values limits can be calculated precisely using ANOVA software. In the case, this work on MB and BG adsorption, Bonferroni limit was 11.7687 and t-value limit was 4.30265. In this plot, any effect bar that exceed t-value limit is significant. And any bar that exceed the more conservative Bonferroni limit, thus providing a high level of confidence – greater than 95% significant. Figures 4.7 and 4.8 offer a simpler view of the relative effects via an ordered bar graph called a “Pareto chart,” which serves as a graphic representation of the effects. This becomes manifest by the significant bars at the left towering over the insignificant bars on the right. Pareto charts provides statistical benchmark for assessing statistical significance of the effects. The vertical axis show the t-value of the absolute effects. The t-value scale provides a more accurate measure of relative size of effects. Any bar that falls below the bottom limit (t-value limit) which is 4.30265 is insignificant. 6 and 7, which are bars for AB and ABC are insignificant effects on MB adsorption.

4.4.4.4 Analysis of variance (ANOVA)

To protect against spurious outcomes, it is absolutely vital to verify the conclusion drawn from the half-normal plots and Pareto charts by doing an analysis of variance (ANOVA) and the associated diagnostics of “residual error”. The probability (“ p-value”) for the model, by default, Design Expert considers values of less than or equal to ($\leq$) 0.05 to be significant. This is the significance threshold risk accepted in this work. From the Table 4.6, p-value for the model 0.0019, and also, p-values for the model terms A, B, C, AC and BC: all pass the 0.005 test with room to spare for both MB and BG ANOVA tables.

Table 4.6: ANOVA report for MB

Response1 **MB adsorption**
ANOVA for selected factorial model
Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model332.63		5	66.53	532.20	0.0019	significant
A-Contact Time	78.12	1	78.12	625.00	0.0016	
B-Dosage	153.12	1	153.12	1225.00	0.0008	
C-pH	45.12	1	45.12	361.00	0.0028	
AC	28.12	1	28.12	225.00	0.0044	
BC	28.13	1	28.13	225.00	0.0044	
Residual	0.25	2	0.12			
Cor Total	332.88	7				

The Model F-value of 532.20 implies the model is significant. There is only a 0.19% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, C, AC, BC are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	0.35	R-Squared	0.9992
Mean	84.88	Adj R-Squared	0.9974
C.V. %	0.42	Pred R-Squared	0.9880
PRESS	4.00	Adeq Precision	64.503

The "Pred R-Squared" of 0.9880 is in reasonable agreement with the "Adj R-Squared" of 0.9974.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 64.503 indicates an adequate signal. This model can be used to navigate the design space.

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	84.88	1	0.12	84.34	85.41	
A-Contact Time	3.12	1	0.12	2.59	3.66	1.00
B-Dosage	4.38	1	0.12	3.84	4.91	1.00
C-pH	2.37	1	0.12	1.84	2.91	1.00
AC	-1.87	1	0.12	-2.41	1.34	1.00
BC	1.88	1	0.12	1.34	2.41	1.00

Final Equation in Terms of Coded Factors:

MB adsorption =
+84.88
+3.12 * A
+4.38 * B
+2.37 * C

-1.87 * A * C
+1.88 * B * C

Final Equation in Terms of Actual Factors:

MB adsorption =
+64.66667
+0.23810 * Contact Time
+0.23810 * Dosage
+0.50000 * pH
-0.017857 * Contact Time * pH
+0.35714 * Dosage * pH

Table 4.7: ANOVA report for BG

Response 2 BG adsorption
ANOVA for selected factorial model
Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	407.00	5	81.40	65.12	0.0152	significant
A-Contact Time	*72.00*	*1*	*72.00*	*57.60*	*0.0169*	
B-Dosage	*180.50*	*1*	*180.50*	*144.40*	*0.0069*	
C-pH	*98.00*	*1*	*98.00*	*78.40*	*0.0125*	
AC	*24.50*	*1*	*24.50*	*19.60*	*0.0474*	
BC	*32.00*	*1*	*32.00*	*25.60*	*0.0369*	
Residual	2.50	2	1.25			
Cor Total	409.50	7				

The Model F-value of 65.12 implies the model is significant. There is only a 1.52% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, C, AC, BC are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	1.12	R-Squared	0.9939
Mean	85.25	Adj R-Squared	0.9786
C.V. %	1.31	Pred R-Squared	0.9023
PRESS	40.00	Adeq Precision	23.238

The "Pred R-Squared" of 0.9023 is in reasonable agreement with the "Adj R-Squared" of 0.9786.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 23.238 indicates an adequate signal. This model can be used to navigate the design space.

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	85.25	1	0.40	83.55	86.95	
A-Contact Time	3.00	1	0.40	1.30	4.70	1.00
B-Dosage	4.75	1	0.40	3.05	6.45	1.00
C-pH	3.50	1	0.40	1.80	5.20	1.00
AC	-1.75	1	0.40	-3.45	-0.049	1.00
BC	2.00	1	0.40	0.30	3.70	1.00

Final Equation in Terms of Coded Factors:

BG adsorption =
+85.25
+3.00 * A
+4.7 * B
+3.50 * C
-1.75 * A * C
+2.00 * B * C

Final Equation in Terms of Actual Factors:

BG adsorption =
+63.16667
+0.22500 * Contact Time
+0.30952 * Dosage
+0.66667 * pH
-0.016667 * Contact Time * pH
+0.38095 * Dosage * pH

4.4.4.5 Modeling response with predictive equations

The model is a mathematical equation used to predict a given response. The factorial crossed model for two factors as given in equation (2.7) is $Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 AB + \beta_5 AC + \beta_6 BC + \beta_7 ABC$. Where Y is the predicted response, β_0 (beta nought) is the intercept, β_1 (beta one) is the model coefficient for the input factor (A) and is also the slope of the line and β_2 (beta two) is the model coefficient for the input factor (B). For statistical purposes, it helps to keep factors in coded form: -1 for low and +1 for high. The fitted model for MB adsorption with the factors of contact time (A), dosage (B) and pH (C) in coded form is

MB adsorption model = 84.88+3.12* A+4.38* B+2.37* C–1.88*A*C + 1.88*B*C (4.2)

BG adsorption model = 85.25+3.00* A+4.75* B+3.50* C–1.75*A*C+2.00*B*C (4.3)

The value for the intercept β_0 of 84.88 and 85.25 represents the average of all actual responses of MB/BG adsorption. The coefficients can be directly compared to assess the relative impact of factors. In this case, we can see that factor AC (coefficient -1.88 and -1.75) causes a bigger negative effect to MB and BG adsorption while factor B, dosage (coefficient + 4.38 and + 4.75) causes bigger positive effect to MB and BG adsorption than factor A, time (coefficient + 3.12 and

+3.00). The one drawback to coded model is that actual factor levels were converted to coded levels before plugging in the input values. Because, using the un-coded model to generate predicted values we make intercept to lose meaning when compared. Also, in the un-coded model, comparing the coefficient of one term with another, such as dosage versus pH make no sense. This project only work with coded model to generate predictive response values. The method used to check this work's model was by entering factor levels from design and generate the predicted response. When the predicted value was compared with the actual (observed) value, a discrepancy or inconsistency was discovered. This discrepancy is called "residual or remaining."

4.4.4.6 Predicted values by manual calculation

Table 4.8: the actual and predicted values

Standard						**MB adsorption**	**MB adsorption**		**BG adsorption**	**BG adsorption**	
	A	B	C	AC	BC	Actual	Predicted	Residual	Actual	Predicted	Residual
1	_	_	_	+	+	75	75	0	75	74.25	0.75
2	+	_	_	_	+	85	85	0	83	83.75	-0.75
3	_	+	_	+	_	80	80	0	79	79.75	-0.75
4	+	+	_	_	_	90	90	0	90	89.25	0.75
5	_	_	+	_	_	80	79.75	0.25	81	80.75	0.25
6	+	_	+	+	_	82	82.25	-0.25	83	83.25	-0.25
7	_	+	+	_	+	92	92.25	-0.25	94	94.25	-0.25

8	+	+	+	+	+	95	94.75	0.25	97	96.75	0.25

The column of predicted values for MB adsorption is determined by plugging the coded factor levels into coded model below. For example, the predicted MB adsorption for standard order 6 is

MB adsorption model = $84.88 + 3.12 * A + 4.38 * B + 2.37 * C - 1.88 * A * C + 1.88 * B * C$

MB adsorption model = $84.88 + 3.12(+1) + 4.38(-1) + 2.37(+1) - 1.88(+1) + 1.88(-1) = 82.23$

Also the predicted MB adsorption for standard order 3 is

MB adsorption model = $84.88 + 3.12(-1) + 4.38(+1) + 2.37(-1) - 1.88(+1) + 1.88(-1) = 80.01$

Also the predicted MB adsorption for standard order 8 is

MB adsorption model = $84.88 + 3.12(+1) + 4.38(+1) + 2.37(+1) - 1.88(+1) + 1.88(+1) = 94.75$

4.4.4.7 MB and BG optimization of interactions

Interactions occur when the effect of one factor depends on the level of the other. The table 4.9 gives the picture of how the factors of experimentation interact with one another.

Effect of contact time and dosage (AB) interaction

Table 4.9: Data of interaction of contact time versus dosage

Standard	Contact time (A)	Dosage (B)	MB adsorption (Average) %
1, 5	_	_	77.5
2, 6	+	_	83.5
3, 7	_	+	86.0

4, 8	+	+	92.5

From Table 4.9, effect of contact time and dosage is insignificant for predicted model development but the interaction effect of AB shows that for optimum dye removal, high contact time must be combined with high dosage to have optimum percentage removal of dyes from wastewater.

Effect of contact time and pH (AC) interaction

Table 4.10: Data of interaction of contact time versus pH

Standard	Contact time (A)	pH (C)	MB adsorption (Average) %
1, 3	_	_	77.5
2, 4,	+	_	87.5
5, 7	_	+	86.0
6, 8	+	+	88.5

From Table 4.10, effect of contact time depends on the level of pH. When pH is low (minus), dye adsorption increase from 77.5 to 87.5. But when pH is high (plus), the dye adsorption increased from 86 to 88.5. This is clearer when graphed as shown below. So, the combination of low contact time and low pH is bad for adsorption while the combination of high contact time and high pH is good for adsorption.

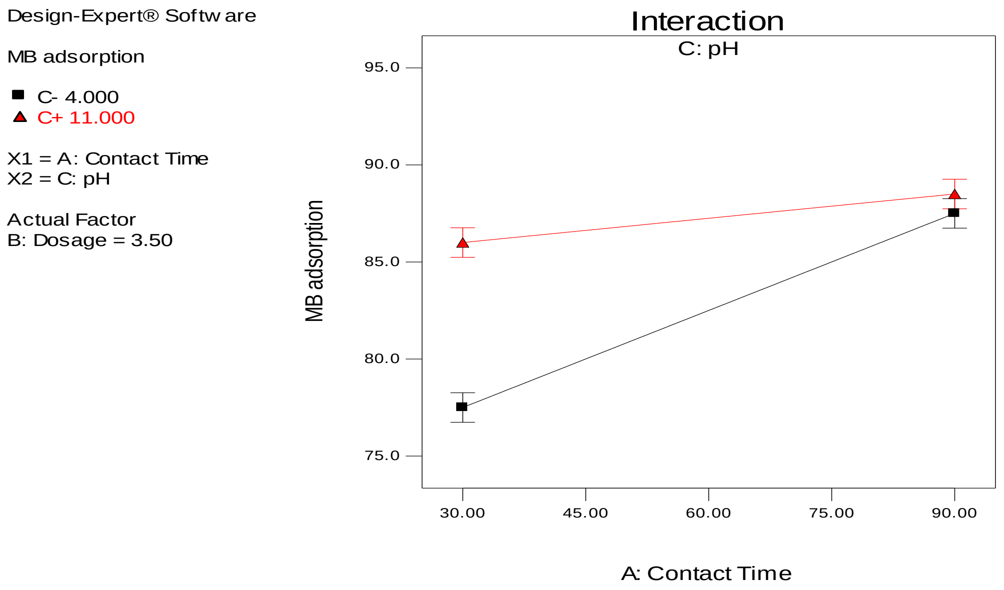

Figure 4.9: Interaction Graph of Contact Time versus pH

Effect of dosage and pH (BC) interaction

Table 4.11: Data of interaction of dosage versus pH

Standard	Dosage (B)	pH (C)	MB adsorption (Average) %
1, 2	_	_	80.0
3, 4	+	_	85.0
5, 6	_	+	81.0
7, 8	+	+	93.5

From Table 4.11, effect of dosage depends on the level of pH. When pH is low (minus), dye adsorption increase from 80 to 85. But when pH is high (plus), the dye adsorption increased from 81 to 93.5. This is clearer when graphed as shown below. So, the combination of low contact time and low pH is bad for adsorption while the combination of high contact time and high pH is good for adsorption.

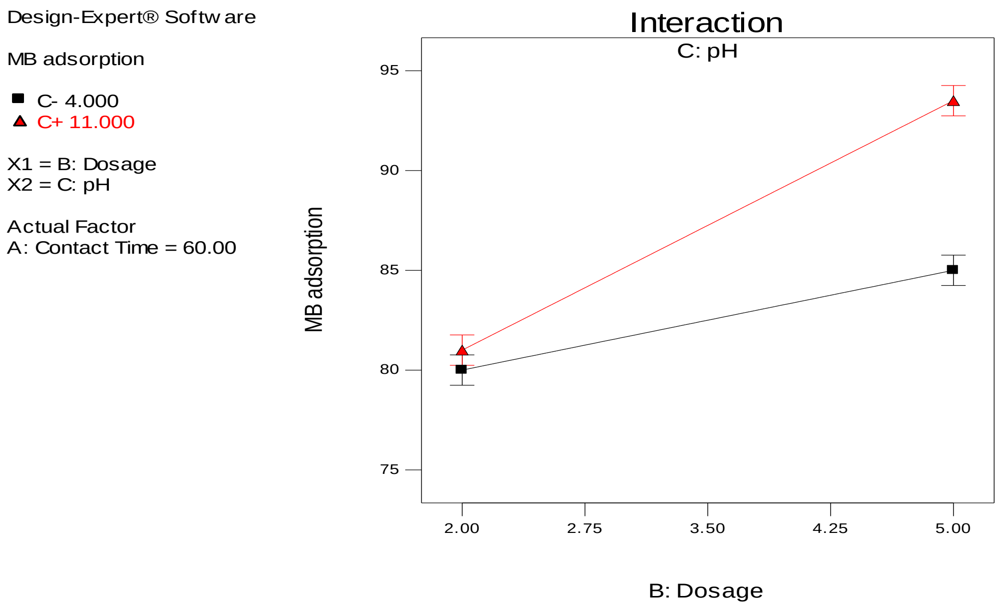

Figure 4.10: Interaction graph of dosage versus pH

The Table 4.11 and the Figure 4.10 show that, for “multi-response optimization” for optimum dye removal, the best setting are high dosage, high contact time and high pH. The Tables 4.12, 4.13, and 4.14 are interaction of factors during BG adsorption. Interactions occur when the effect of one factor depends on the level of the other. The Table 4.12 gives the picture of how the factors of experimentation interact with one another.

Effect of contact time and dosage (AB) interaction

Table 4.12: Data of interaction of contact time versus dosage

Standard	Contact time (A)	Dosage (B)	BG adsorption (Average) %

1, 5	_	_	78.0
2, 6	+	_	83.0
3, 7	_	+	86.5
4, 8	+	+	93.5

From Table 4.12, the effect of contact time and dosage is insignificant for predicted model development but the interaction effect of AB shows that for optimum dye removal, high contact time must be combined with high dosage.

Effect of contact time and pH (AC) interaction

Table 4.13: Data of interaction of contact time versus pH

Standard	**Contact time (A)**	**pH (C)**	**BG adsorption (Average) %**
1, 3	_	_	77.0
2, 4,	+	_	86.5
5, 7	_	+	87.5
6, 8	+	+	90.0

From Table 4.13, effect of contact time depends on the level of pH. When pH is low (minus), dye adsorption increase from 77.0 to 86.5. But when pH is high (plus), the dye adsorption increased from 87.5 to 90. This is clearer when graphed as shown below. So, the combination of low contact time and low pH is bad for adsorption while the combination of high contact time and high pH is good for adsorption.

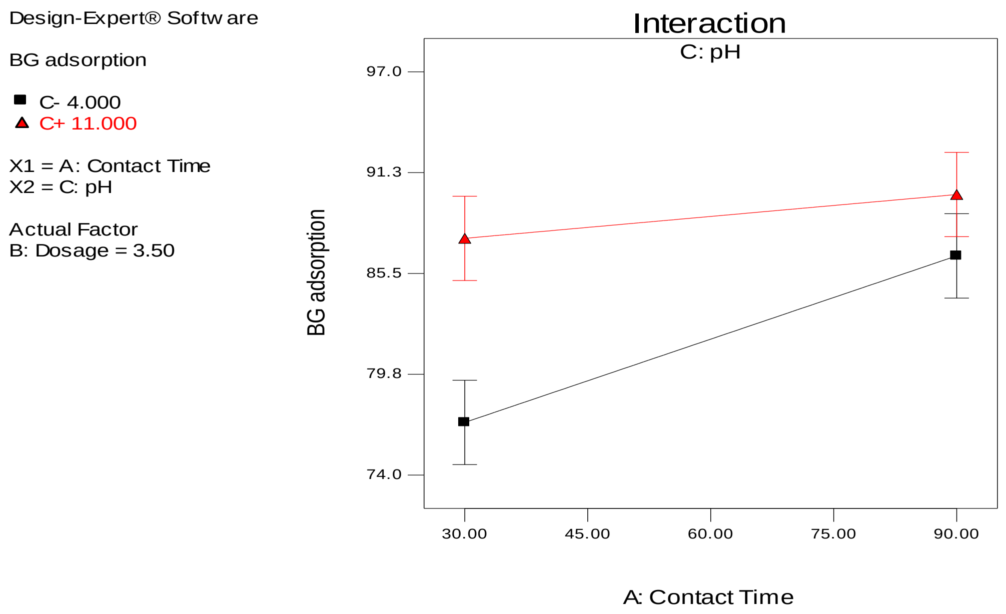

Figure 4.12: Interaction graph of dosage versus pH

Effect of dosage and pH (BC) interaction

Table 4.14: Data of interaction of dosage versus pH

Standard	Dosage (B)	pH (C)	BG adsorption (Average) %
1, 2	_	_	79.0
3, 4	+	_	84.5
5, 6	_	+	82.0
7, 8	+	+	95.5

From Table 4.14, effect of dosage depends on the level of pH. When pH is low (minus), dye adsorption increase from 79 to 84.5. But when pH is high (plus), the dye adsorption increased from 82 to 95.5. This is clearer when graphed as shown below. So, the combination of low contact time and low pH is bad for adsorption while the combination of high contact time and high pH is good for adsorption.

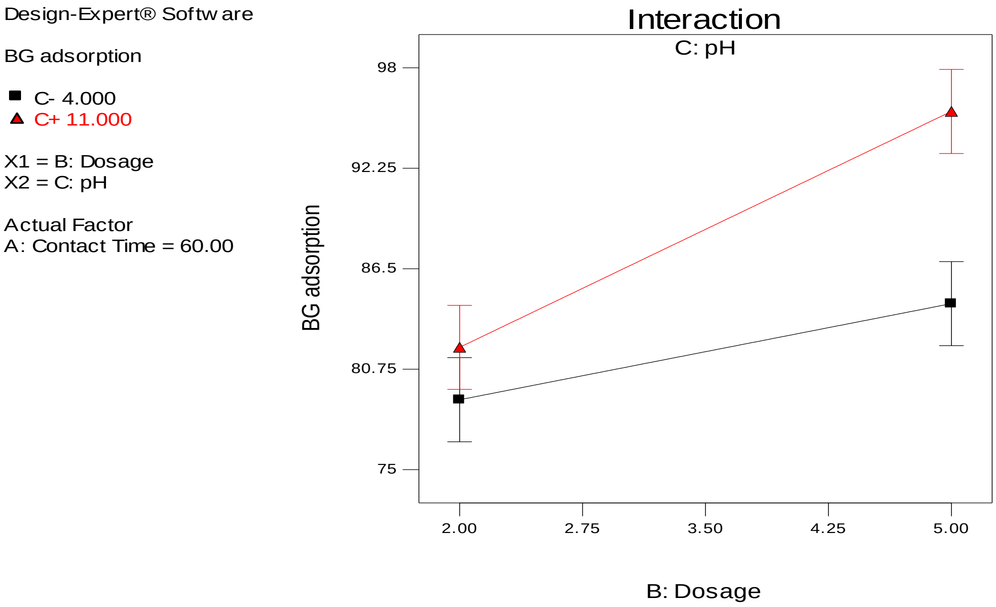

Figure 4.13: Interaction graph of dosage versus pH

The Tables 4.12, 4.13, 4.14 and the Figures 4.11, 4.12, 4.13 show that, for “multi-response optimization” for optimum dye removal, the best setting are high dosage, high contact time and high pH.

4.5 Isotherm models

4.5.1: Langmuir isotherm plots

The Langmuir isotherm was evaluated using the model (equation 2.5) and the results are presented in figures 4.14 – 4.17.

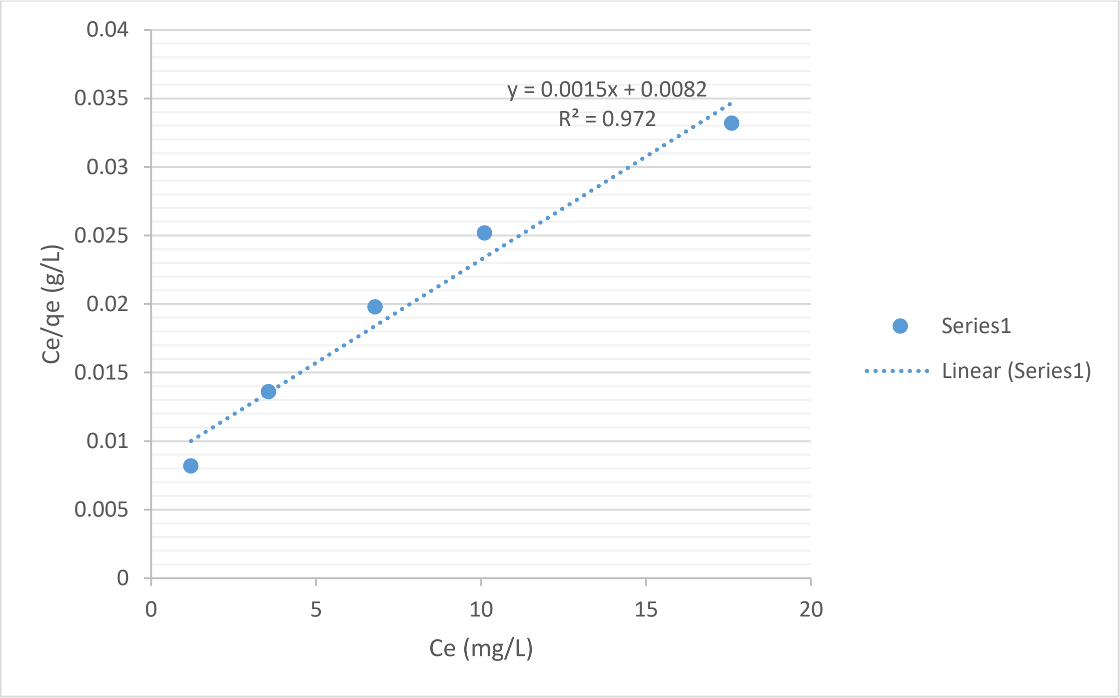

Figure 4.14: Langmuir isotherm of methylene blue unto coconut shell AC

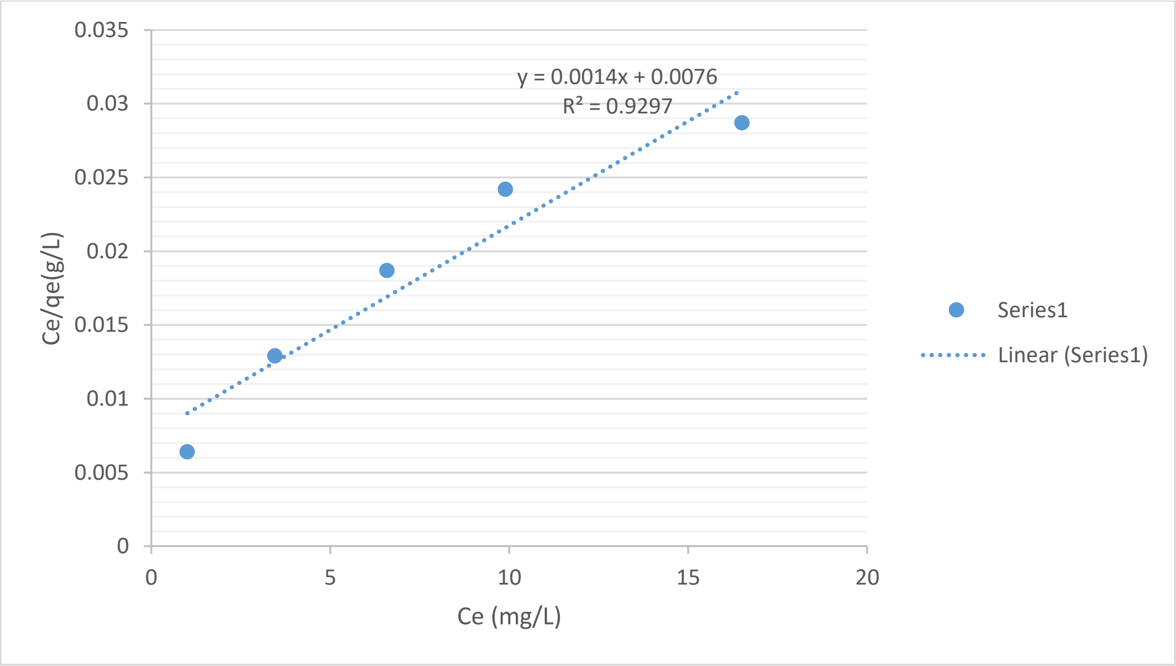

Figure4.15: Langmuir isotherm of methylene blue unto eucalyptus tree AC

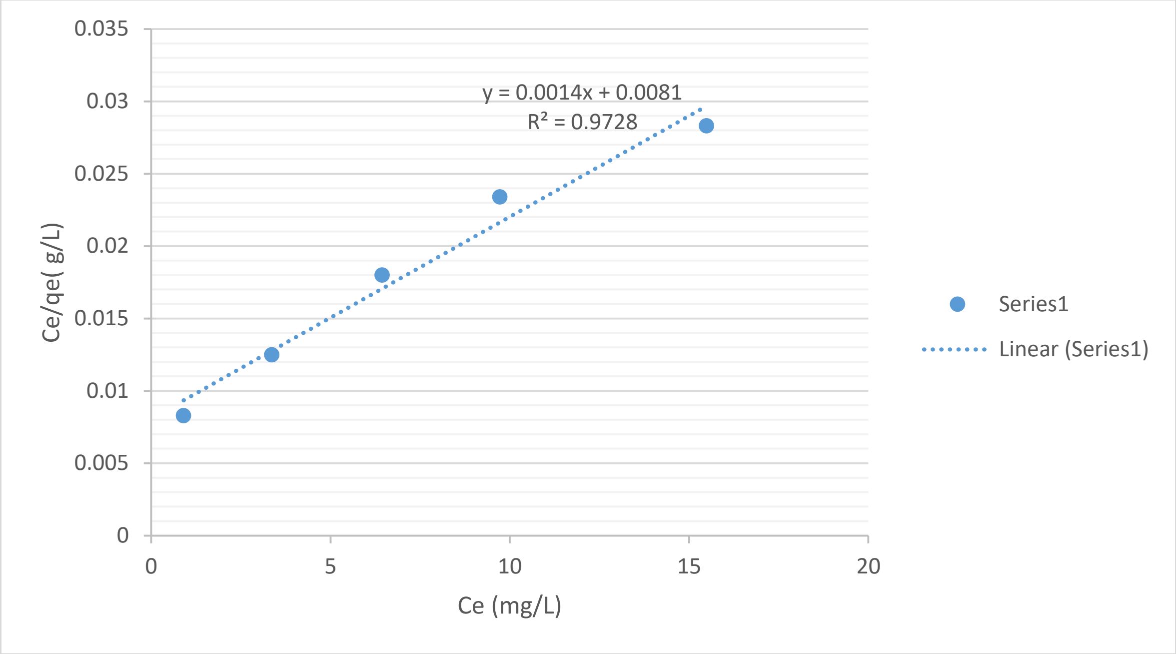

Figure 4.16: Langmuir isotherm of methylene blue unto flamboyant pod AC

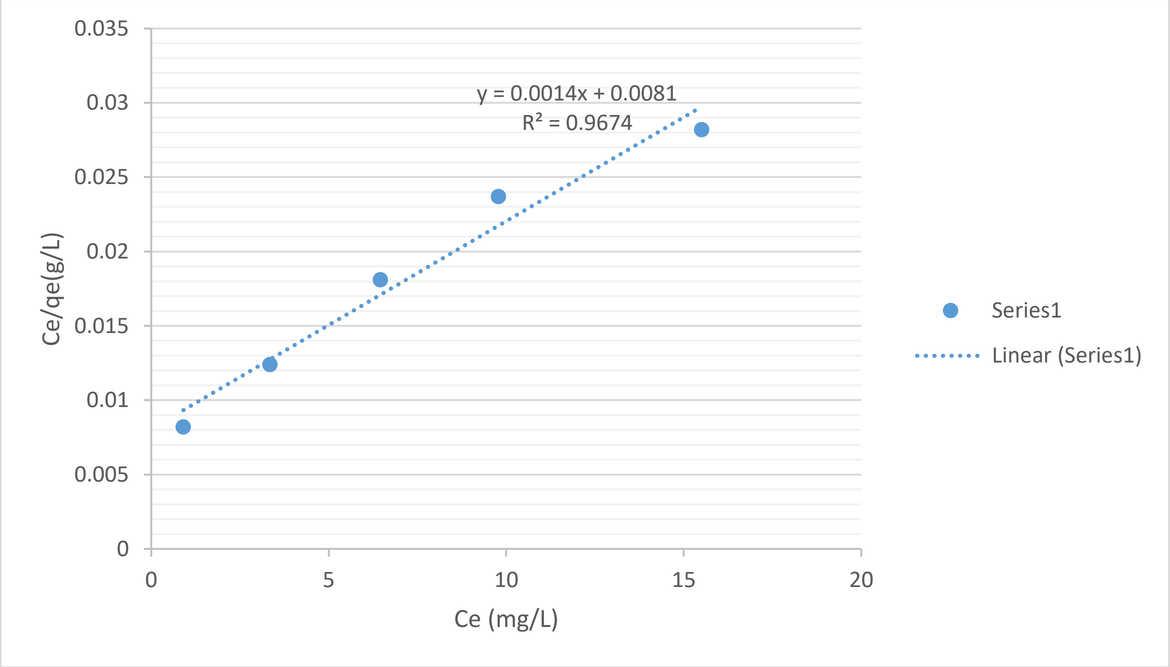

Figure 4.17: Langmuir isotherm of methylene blue unto corn cob AC

4.5.2: Freundlich isotherm plots

From equation 2.3, the Freundlich model is described by $q_e = K_F C_e^{1/n}$, when equation 2.3 was linearized, it becomes $\text{Log } q_e = \log K_f + 1/n \log C_e$ in equation (2.4). A plot of $\log q_e$ versus $\log C_e$ is a straight line with the interception at y-axis representing the value of $\log K_F$ with slope $1/n$.

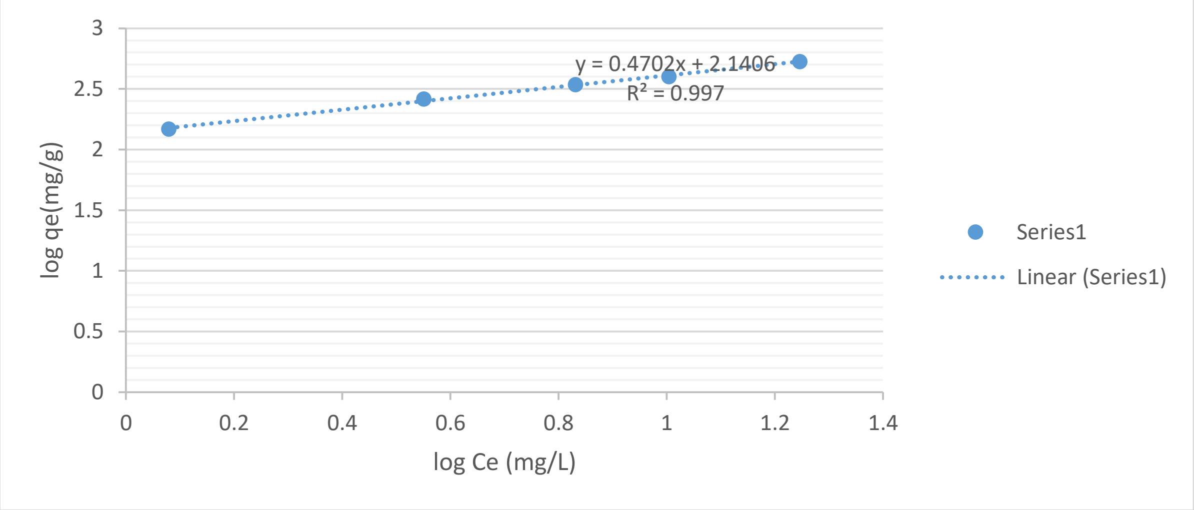

Figure 4.18: Freundlich isotherm of methylene blue unto coconut shell AC

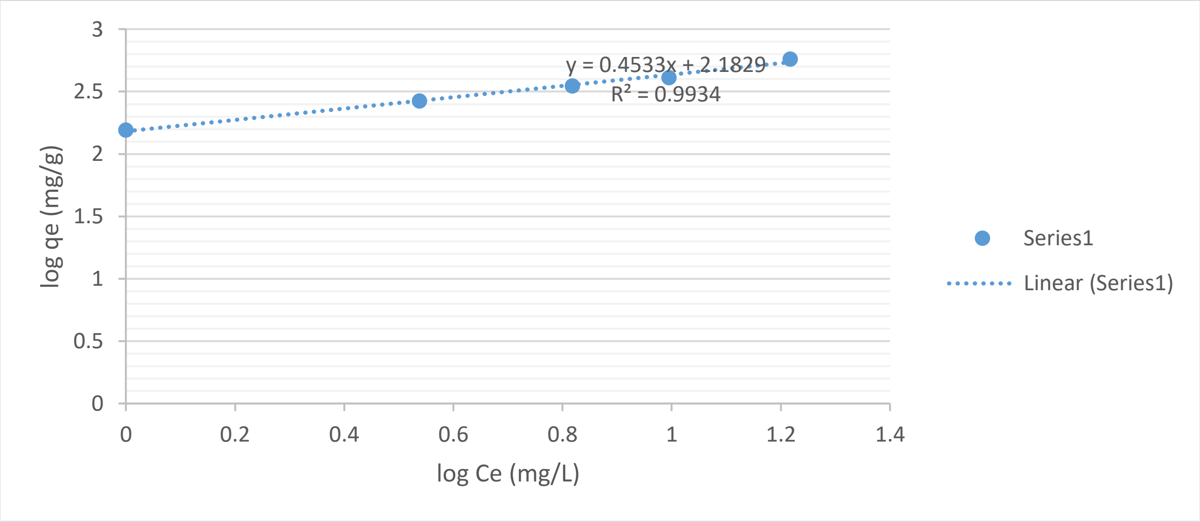

Figure 4.19: Freundlich isotherm of methylene blue unto eucalyptus tree AC

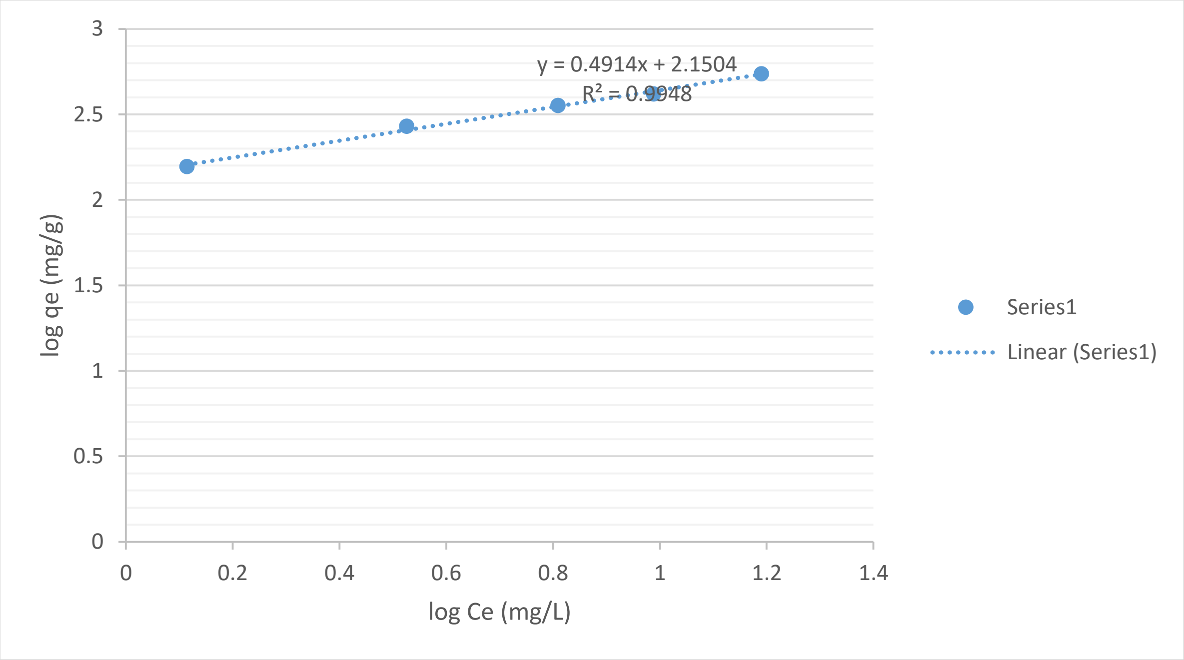

Figure 4.20: Freundlich isotherm of methylene blue unto flamboyant pod AC

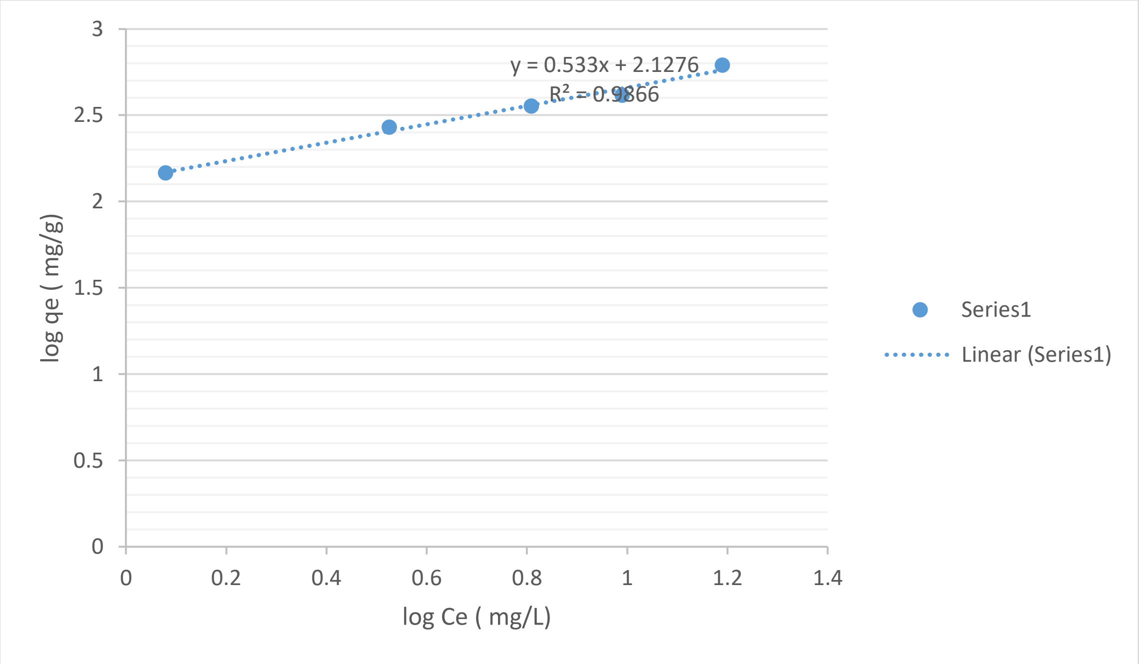

Figure 4.21: Freundlich Isotherm of methylene blue unto corn cob activated carbons

Table 4.15: Freundlich and Langmuir data

	Freundlich			Langmuir			
Adsorbents	$\frac{1}{n}$	k_f (mg/g)	R^2	b (L/mg)	a (mg/g)	R^2	R_L
Coconut shell	0.417	2.13	0.9970	0.0013	0.008	0.9720	0.961
Eucalyptus tree	0.385	2.15	0.9934	0.0015	0.007	0.9297	0.955
Corn cob	0.388	2.10	0.9948	0.0014	0.008	0.9674	0.958
Flamboyant pod	0.444	2.10	0.9866	0.0014	0.009	0.9728	0.958

The linear plots of Ce/qe against Ce, are shown in Figures 4.18, 4.19, 4.20 and 4.21. The values of K_f (mg/g) and b (L/mg) are shown in the Table 4.15 were determined for all adsorbents from intercept and slopes of the linear plots. The shape of the Langmuir isotherm were investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption. R_L was calculated using equation (2.6). In the present investigation, the R_L values were less than one for MB concentration range studied, which shows the adsorption process was favourable. Similarly, the linear plot of Freundlich isotherm showed the applicability of all adsorbents. The value of 1/n which is closer to 0 means the adsorption is more heterogeneous. A value for $1/n$ below one indicates a normal Freundlich isotherm while $1/n$ above one is an indicative of cooperative adsorption or ($1/n = 0$), favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$). From the experimental data the value of 1/n was less than one indicating the favourable adsorption and heterogeneous adsorption. The applicability of the two isotherms were compared by evaluating the correlation coefficients R^2, and based on the correlation coefficient from the two isotherm models, freundlich model gave the highest R^2 value showing that the adsorption of MB onto adsorbents used in this present work was best described by this model. The higher correlation coefficient for the Langmuir model predicts the coverage of MB may be monolayer and homogenous adsorption but the model is best fitted in freundlich model. Moreover the R_L values were less than one which shows the adsorption process was favourable.

4.6 Column adsorption studies by factorial method

The table 4.16 shows the template used for the column experiments carried out using factorial method

Table 4.16: Column experiment factorial method template

Number of runs	A	B	C	Flow rate (ml /mins)	Adsorbent mass (g)	pH
1	_	_	_	4.3	10.6	4
2	+	_	_	8.6	10.6	4
3	_	+	_	4.3	15.9	4
4	+	+	_	8.6	15.9	4
5	_	_	+	4.3	10.3	11
6	+	_	+	8.6	10.3	11
7	_	+	+	4.3	15.9	11

8	+	+	+	8.6	15.9	11

4.7 Column adsorption experimental data

Table 4.17: MB Column data obtained using factorial method

Number of runs	Breakpoint time tb (min)	Final conc. (mg/L)	MB removal (%)
1	14	0.001866	37.8
2	14	0.001794	40.2
3	17.5	0.001839	38.7
4	17.5	0.001767	41.1
5	14	0.001800	40.0
6	14	0.001773	40.9
7	14	0.001659	44.7
8	14	0.001683	43.9

Table 4.18: BG Column data obtained using factorial method

Number of runs	**Breakpoint time tb (min)**	**Final conc. (mg/L)**	**BG removal (%)**
1	14	0.001806	39.8
2	14	0.001767	41.1
3	17.5	0.001809	39.7
4	17.5	0.001737	42.1
5	14	0.001800	40.0
6	14	0.001722	42.6
7	14	0.001626	45.8
8	14	0.001659	44.7

4.8: Analysis of column studies by factorial design

After entering the responses data from column studies in Tables 4.17 and 4.18 design layout in standard order, and the analysis was carried out by looking at a half-normal plot of the estimated effects of MB adsorption and BG adsorption as shown in Figure 4.22 and 4.23.

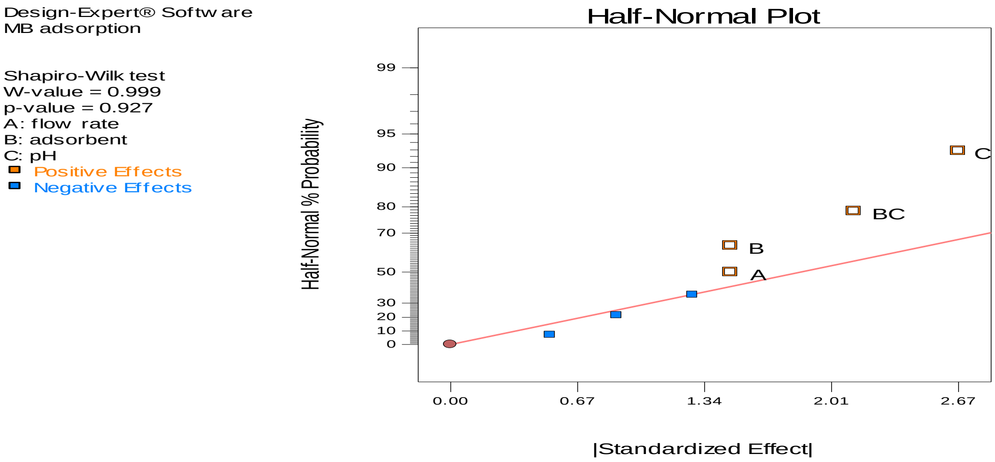

Figure 4.22: Half normal plot for MB adsorption in column studies

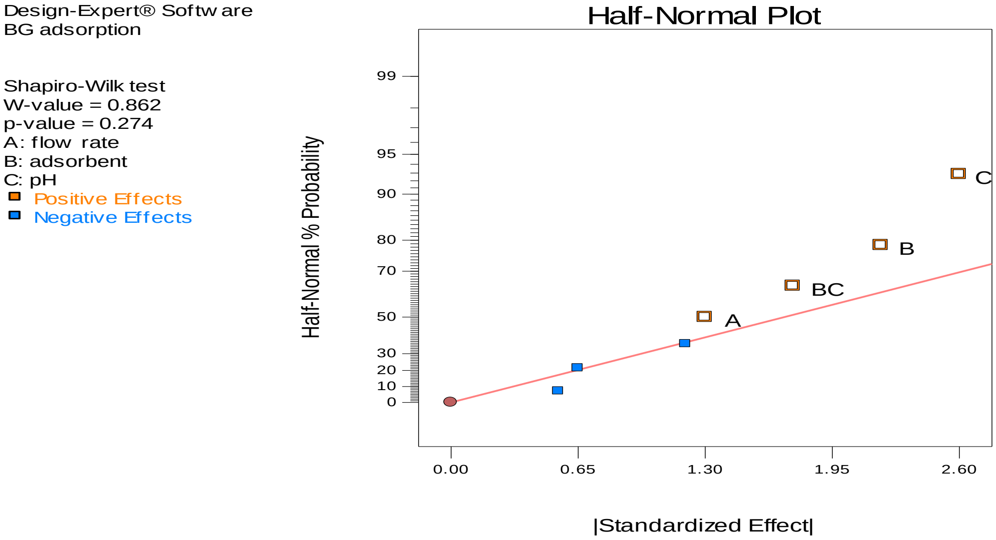

Figure 4.23: Half normal plot for BG adsorption in column studies

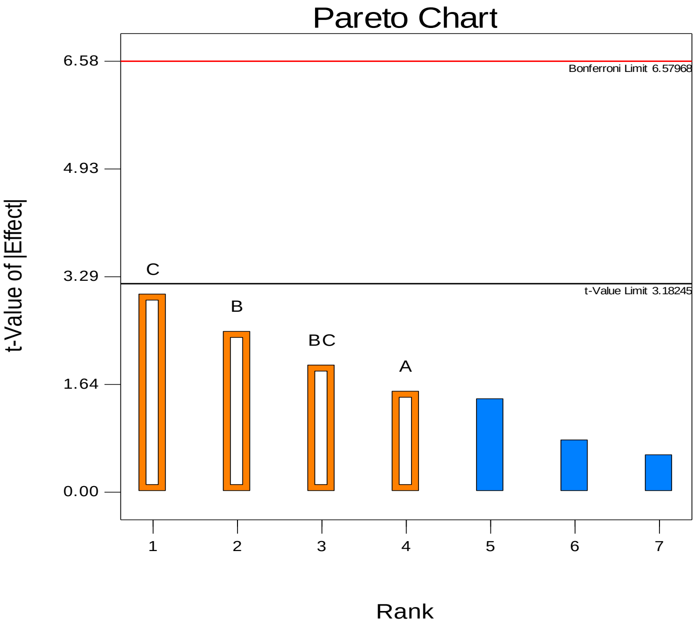

Figure 4.24: Pareto chart in column studies

From Figures 4.22, 4.23 and 4.24, we discovered that the variation in the responses is probably driven by the C (pH) effect. Effect A, B and interaction between B and C also play roles in the variation in the responses, but it is C effect that has the biggest effect on the variation in the responses. To check the effects that is involved in the significant interaction, ANOVA analysis was performed as shown below. From the ANOVA Table 4.19, the "Model F-value" of 4.51 implies the model for MB adsorption is not significant relative to the noise. There is a 12.32 % chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant. In statistical sense, there is no effective interaction in the main effects, and this resulted into a model that is trivial.

Table 4.19: MB anova model terms

Standard Deviation	Mean	C.V. %	Press	R-Squared	Adj R-Squared	Pred R-Squared	Adeq Precision
1.33	41.56	3.21	37.93	0.8573	0.6670	0.0147	5.953

similarly, the BG adsorption Model F-value of 5.66 implies there is a 9.29% chance that a "Model F-Value" this large could occur due to noise.Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Table 4.20: BG anova model terms

Standard Deviation	Mean	C.V. %	Press	R-Squared	Adj R-Squared	Pred R-Squared	Adeq Precision
1.20	41.98	2.86	30.79	0.8831	0.7272	0.1686	6.423

The "Pred R-Squared" of 0.1686 is not as close to the "Adj R-Squared" of 0.7272 as one mightnormally expect. This may indicate a large block effect or a possible problem with the model and/or data generated during experiment. The insignificancy of these models indicate that there is no effective interaction between the main effects. This might have happened evidently due to normal causes – presumably as a result of experimental error (noise in the system). The experimental error possibly explained why there is block effect, that is, there is no proper and interaction between main effects leading to the generation of data that is useful for the proper analysis of interaction effects using design expert tools. The experimental set up of the column studies and the experiments itself is not as effective as batch experiments carried out during the cause of this work. There is no adequate equipments which could be used to carried out column experiment in the resarch laboratories in most of our universities, as they are available in foreign universities and reaserches centres.

4.9 Interpretation and optimization of interaction effects

Interactions occur when the effect of one factor depends on the level of the other.

Effect of flow rate and adsorbent mass (AB) interaction

Table 4.21: Data of interaction of flow rate versus adsorbent mass

Standard	Flow rate (A)	Adsorbent mass (B)	MB adsorption (Average) %
1, 5	_	_	39.9
2, 6	+	_	40.6
3, 7	_	+	41.7
4, 8	+	+	42.5

Effect of contact flow rate and pH (AC) interaction

Table 4.22: Data of interaction of flow rate versus pH

Standard	Flow rate	pH	MB adsorption

	(A)	(C)	(Average) %
1, 3	_	_	38.3
2, 4,	+	_	40.1
5, 7	_	+	42.35
6, 8	+	+	42.4

From Tables 4.21 and 4.22, the effect of contact time and flow rate depend on the level of pH. When pH is low (minus), dye adsorption increase from 39.9 to 40.6 and from 38.3 to 40.1. But when pH is high (plus), the dye adsorption increased from 41.7 to 42. And 42.35 to 42.4. These optimization shows the poor interaction between the flow rate and contact time against pH.

Effect of adsorbent mass and pH (BC) interaction

Table 4.23: data of interaction of adsorbent mass versus pH

Standard	Adsorbent mass (B)	pH (C)	MB adsorption (Average) %
1, 2	_	_	39.0
3, 4	+	_	39.9
5, 6	_	+	40.5
7, 8	+	+	44.3

From the Table 4.23, effect of adsorbent mass depends on the level of pH. For example, when pH is low (minus), MB adsorption % removal increased from 39.0 to 39.9. But when pH is high (+), MB adsorption % removal increased from 40.5 to 44.3 percent. This is clearer when graphed as below.

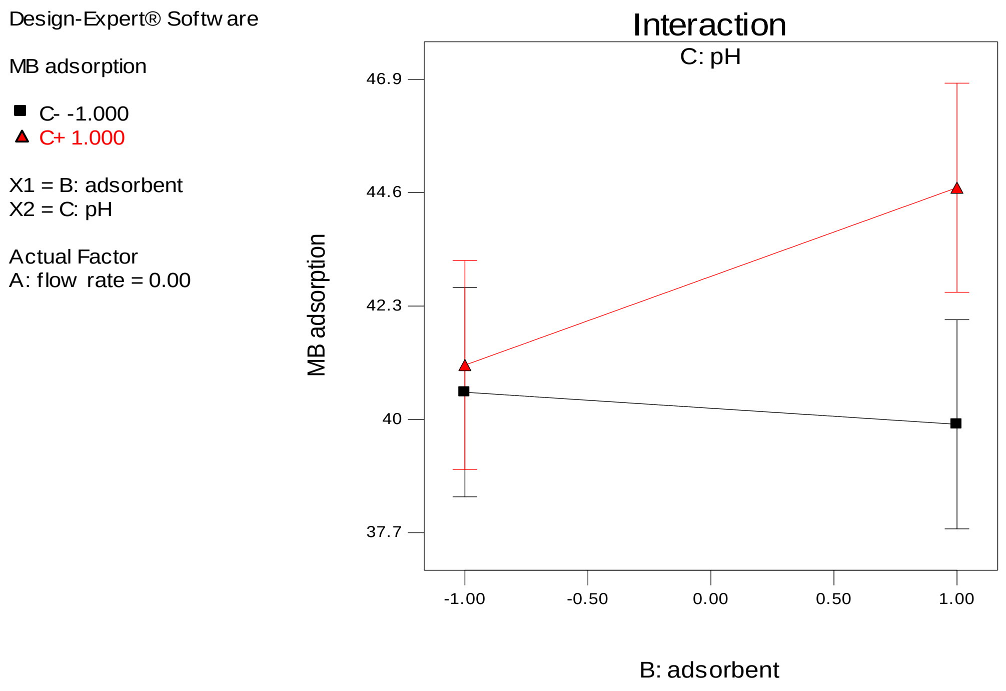

Figure 4.25: interaction graph of adsorbent mass versus pH

Effect of adsorbent mass and pH (BC) interaction

Table 4.24: data of interaction of adsorbent mass versus pH

Standard	Adsorbent mass (B)	pH (C)	BG adsorption (Average) %
1, 2	_	_	40.45
3, 4	+	_	40.9
5, 6	_	+	41.3
7, 8	+	+	45.25

From the Table 4.24, effect of adsorbent mass depends on the level of pH. For example, when pH is low (minus), BG adsorption % removal increased from 40.45 to 40.9. But when pH is high (+), BG adsorption % removal increased from 41.3 to 45.25 percent. This is clearer when graphed as below

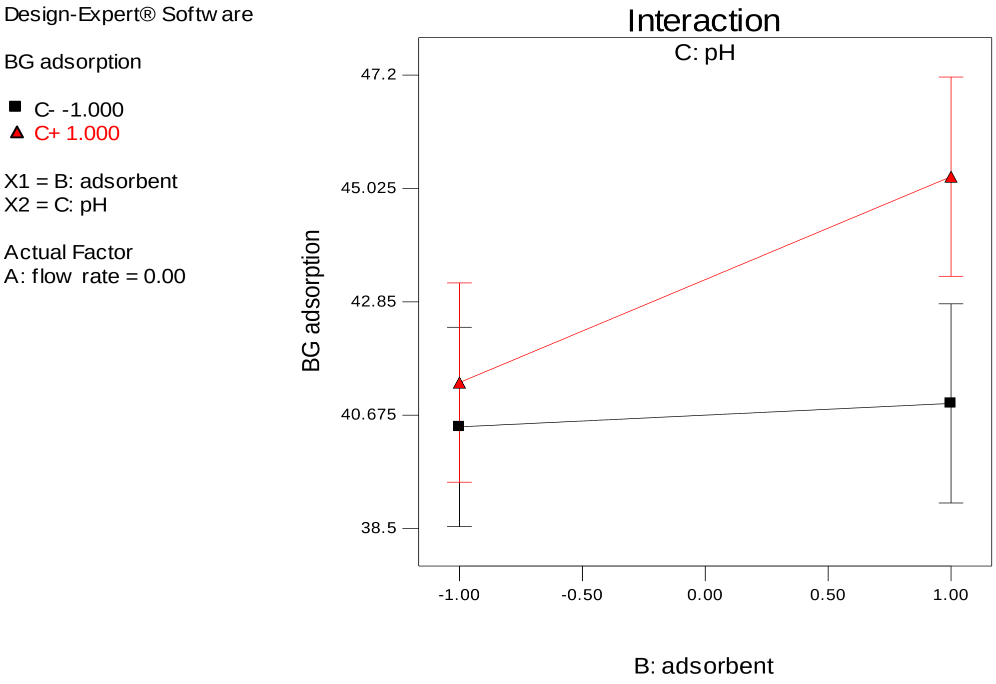

Figure 4.26: interaction graph of adsorbent mass versus pH

The Tables 4.23, 4.24 and the Figures 4.25 4.26 show that, for “multi-response optimization” of MB adsorption and BG adsorption, the best setting are high adsorbent mass and high pH. And, flow rate is a trivial factor because it has no effect on the interaction.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based on the study, it can be concluded that:

- The adsorption data for the batch process fitted into Langmuir and freundlich Isotherms, and freundlich adsorption isotherm was found to have the highest coefficient of determination, hence gave the best fit.
- The pH of the adsorbate, contact time and adsorbent dosage are highly responsible for dyes removal from wastewater
- Experimental data were examined using analysis of variance (ANOVA), t-test, and Bonferroni - test. According to Pareto Chart, ANOVA, main effects and interaction plots in design expert, the most significant factors on removal efficiency (%) was found to be adsorbent dosage.
- Due to the obtained results, it can be concluded that modified carbons which were produced by chemical activation of carbonized coconut shell, eucalyptus tree, corn cob and flamboyant pod could be employed as an effective and low-cost adsorbent for the removal of dyes from wastewater.

5.2 Recommendations

The following recommendations are necessary for future research

- ✓ Factorial design for batch adsorption experiment should be encouraged because it helps to optimize operation parameters to determine the best condition for optimum percentage removal.
- ✓ Peristaltic pump is a necessity for column studies and should be made available in the laboratories.

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APPENDIX A

MAIN AND INTERACTION EFFECTS DATA

MB main and interaction effects:

Factor A: Effect = $\frac{85+92+80+80}{4} - \frac{75+90+82+95}{4}$ = 84.25 – 85.5 = - 1.25

Factor B: Effect = $\frac{90+92+95+80}{4} - \frac{75+85+82+80}{4}$ = 89.25 – 80.5 = 8.75

Factor C: Effect = $\frac{82+80+95+80}{4} - \frac{75+85+90+92}{4}$ = 84.25 – 85.5 = -1.25

Factor AB: Effect = $\frac{75+90+80+95}{4} - \frac{85+80+82+92}{4}$ = 85 – 84.75 = 0.25

Factor AC: Effect = $\frac{75+80+92+95}{4} - \frac{92+85+90+80}{4}$ = 85.5 – 86.75 = -1.25

Factor BC: Effect = $\frac{75+85+92+95}{4} - \frac{80+82+90+80}{4}$ = 86.75 – 83 = 3.75

Factor ABC: Effect = $\frac{85+80+80+95}{4} - \frac{75+90+82+92}{4}$ = 85 – 84.75 = 0.25

BG main and interaction effects:

Factor A: Effect = $\frac{83+90+83+97}{4} - \frac{75+79+81+94}{4}$ = 88.25 – 82.25 = 6.0

Factor B: Effect = $\frac{79+90+94+97}{4} - \frac{75+83+81+83}{4}$ = 90.00 – 80.5 = 9.5

Factor C: Effect = $\frac{81+83+94+97}{4} - \frac{75+83+79+90}{4}$ = 88.75 – 81.75 = 7.0

Factor AB: Effect = $\frac{75+90+81+97}{4} - \frac{83+79+83+94}{4}$ = 85.75 – 84.75 = 1.0

Factor AC: Effect = $\frac{75+79+83+97}{4} - \frac{83+81+90+94}{4}$ = 83.5 – 87 = -3.5

Factor BC: Effect = $\frac{75+83+94+97}{4} - \frac{79+81+90+83}{4}$ = 87.25 – 83.25 = 4.0

APPENDIX B

MB AND BG ADSORPTION EXPERIMENTAL DATA

Table 1: MB Adsorption by Eucalyptus tree

Number of runs	Final conc. using activated carbon	% removal by activated carbon	Final conc. using raw carbon	% removal by raw carbon
1	0.001129	62.4	0.001398	47.4
2	0.000869	71.0	0.001047	60.1
3	0.000721	75.9	0.001026	62.8
4	0.000559	81.4	0.000717	65.1
5	0.000218	92.7	0.000438	72.4
6	0.000188	93.7	0.000357	75.1
7	0.000284	90.5	0.000474	69.2

8	0.000203	93.2	0.000408	70.4

Table 2: MB Adsorption by corn cob

Number of runs	Final conc. using activated carbon	% removal by activated carbon	Final conc. using raw carbon	% removal by raw carbon
1	0.000107	96.4	0.000264	74.2
2	0.000746	99.9	0.000894	76.2
3	0.000025	99.2	0.000216	75.8
4	0.000633	78.9	0.000948	58.4
5	0.000196	93.5	0.000291	68.3
6	0.000196	93.5	0.000303	70.9
7	0.000233	92.2	0.000438	67.4
8	0.000151	94.9	0.000297	72.1

Table 3: MB adsorption by flamboyant pod

Number of runs	Final conc. using activated carbon	% removal by activated carbon	Final conc. using raw carbon	% removal by raw carbon
1	0.000078	97.4	0.000417	69.1
2	0.000099	99.7	0.000447	64.1
3	0.000033	99.4	0.000318	75.4
4	0.000314	89.5	0.000588	63.4

5	0.000033	98.2	0.000375	74.5
6	0.000114	96.2	0.000345	63.5
7	0.000262	91.3	0.000597	60.1
8	0.000166	94.5	0.000537	63.1

Table 4: BG adsorption by eucalyptus tree

Number of runs	Final conc. using activated carbon	% removal by activated carbon	Final conc. using raw carbon	% removal by raw carbon
1	0.001111	62.9	0.001323	51.9
2	0.000613	79.6	0.000888	59.4
3	0.000332	88.9	0.000606	71.8
4	0.000153	94.9	0.000408	73.4
5	0.000581	80.6	0.000738	64.4
6	0.000355	88.2	0.000648	70.4
7	0.000168	94.4	0.000042	72.0
8	0.000059	98.0	0.000354	74.9

Table 5: BG adsorption by corn cob

Number of runs	Final conc. using activated carbon	% removal by activated carbon	Final conc. using raw carbon	% removal by raw carbon
1	0.000028	99.1	0.000237	75.1
2	0.000020	99.3	0.000204	76.0
3	0.000044	98.5	0.000294	72.2
4	0.000239	92.0	0.000408	65.4
5	0.000028	99.1	0.000246	74.8
6	0.000036	98.8	0.000324	69.2
7	0.000051	98.3	0.000411	68.3
8	0.000012	99.6	0.000153	76.1

Table 6: BG adsorption by flamboyant pod

Number of runs	Final conc. using activated carbon	% removal by activated carbon	Final conc. using raw carbon	% removal by raw carbon
1	0.000012	99.6	0.000315	72.5
2	0.000044	98.5	0.000405	66.5
3	0.000051	98.3	0.000348	64.4
4	0.000028	99.1	0.000300	72.0
5	0.000090	97.0	0.000438	63.4

6	0.000036	98.8	0.000366	65.8
7	0.000044	98.5	0.000474	70.2
8	0.000831	98.5	0.001173	60.9

APPENDIX C

EXPERIMENTAL DATA FOR MB AND BG DYES

Results obtained for MB

Table 1: run 1, Q = 4.3ml/mins, pH 4 and adsorbent mass = 10.6g

Sample collected	MB Final conc.	MB % removal	Breakpoint time(minutes)
1	0.001866	37.8	
2	0.002262	24.6	
3	0.002388	20.4	
4	0.002883	3.9	14.0
5	0.002886	3.8	
6	0.002913	2.9	

Table 2: run 2, Q = 8.6ml/mins, pH 4 and adsorbent mass = 10.6g

Sample collected	MB Final conc.	MB % removal	Breakpoint time(minutes)
1	0.001794	40.2	
2	0.001956	34.8	
3	0.002655	11.5	
4	0.002913	2.7	14.0
5	0.002925	2.5	
6	0.002937	2.1	

Table 3: run 3, Q = 4.3ml/mins, pH 4 and adsorbent mass = 15.9g

Sample collected	MB Final conc.	MB % removal	Breakpoint time(minutes)
1	0.001836	38.8	
2	0.002037	32.1	
3	0.002130	29.0	
4	0.002760	8.0	
5	0.002922	2.6	17.5

6	0.002940	2.0	

Table 4: run 4, Q = 8.6ml/mins, pH 4 and adsorbent mass = 15.9g

Sample collected	MB Final conc.	MB % removal	Breakpoint time(minutes)
1	0.001767	41.1	
2	0.001962	34.6	
3	0.002223	25.9	
4	0.002685	10.5	
5	0.002937	2.1	17.5
6	0.002946	1.8	

Table 5: run 5, Q = 4.3ml/mins, pH 11 and adsorbent mass = 10.6g

Sample collected	MB Final conc.	MB % removal	Breakpoint time(minutes)
1	0.001800	40.0	

2	0.002181	27.3	
3	0.002610	13.0	
4	0.002940	2.0	14
5	0.002946	1.8	
6	0.002955	1.5	

Table 6: run 6, Q = 8.6ml/mins, pH 11 and adsorbent mass = 10.6g

Sample collected	MB Final conc.	MB % removal	Breakpoint time(minutes)
1	0.001773	40.9	
2	0.002118	29.4	
3	0.002691	10.3	
4	0.002931	2.3	14
5	0.002940	2.0	
6	0.002955	1.5	

Table 7: run 7, Q = 4.3ml/mins, pH 11 and adsorbent mass = 15.9g

Sample collected	MB Final conc.	MB % removal	Breakpoint time(minutes)
1	0.001659	44.7	
2	0.002229	25.7	
3	0.002640	12.0	
4	0.002919	2.7	14
5	0.002934	2.2	
6	0.002946	1.8	

Table 8: run 8, Q = 4=8.6ml/mins, pH 11 and adsorbent mass = 15.9g

Sample collected	MB Final conc.	MB % removal	Breakpoint time(minutes)
1	0.001683	43.9	
2	0.001983	33.9	
3	0.002643	11.9	
4	0.002886	3.8	14

5	0.002928	2.4	
6	0.002940	2.0	

Results obtained for BG

Table 9: run 1, Q = 4.3ml/mins, pH 4 and adsorbent mass = 10.6g

Sample collected	**BG Final conc.**	**BG % removal**	**Breakpoint time (minutes)**
1	0.001806	39.8	
2	0.002148	28.4	
3	0.002688	10.4	
4	0.002898	3.4	14
5	0.002913	2.9	
6	0.002922	2.6	

Table 10: run 2, Q = 8.6ml/mins, pH 4 and adsorbent mass = 10.6g

Sample collected	**BG Final conc.**	**BG % removal**	**Breakpoint time (minutes)**
1	0.001767	41.1	
2	0.001980	34.0	
3	0.002544	15.2	
4	0.002898	3.4	14
5	0.002907	3.1	
6	0.002916	2.8	

Table 11: run 3, Q = 4.3ml/mins, pH 4 and adsorbent mass = 15.9g

Sample collected	**BG Final conc.**	**BG % removal**	**Breakpoint time(minutes)**
1	0.001809	39.7	
2	0.002223	25.9	
3	0.002481	17.3	

4	0.002658	11.4	
5	0.002910	3.0	17.5
6	0.002913	2.9	

Table 12: run 4, Q = 8.6ml/mins, pH 4 and adsorbent mass = 15.9g

Sample collected	**BG Final conc.**	**BG % removal**	**Breakpoint time(minutes)**
1	0.001737	42.1	
2	0.001929	35.7	
3	0.002556	14.8	
4	0.002715	9.5	
5	0.002940	2.0	17.5
6	0.002946	1.8	

Table 13: run 5, Q = 4.3ml/mins, pH 11 and adsorbent mass = 10.6g

Sample collected	**BG Final conc.**	**BG % removal**	**Breakpoint time (minutes)**
1	0.001800	40.0	
2	0.002229	25.7	
3	0.002511	16.3	
4	0.002940	2.0	14
5	0.002946	1.8	
6	0.002949	1.7	

Table 14: run 6, Q = 8.6ml/mins, pH 11 and adsorbent mass = 10.6g

Sample collected	**BG Final conc.**	**BG % removal**	**Breakpoint time (minutes)**
1	0.001722	42.6	
2	0.002037	32.1	
3	0.002607	13.9	
4	0.002883	3.9	14

5	0.002898	3.4	
6	0.002913	2.9	

Table 15: run 7, Q = 4.3ml/mins, pH 11 and adsorbent mass = 15.9g

Sample collected	BG Final conc.	BG % removal	Breakpoint time(minutes)
1	0.001626	45.8	
2	0.001938	35.4	
3	0.002478	17.4	
4	0.002913	2.9	14
5	0.002919	2.7	
6	0.002928	2.4	

Table 16: run 8, Q = 8.6ml/mins, pH 11 and adsorbent mass = 15.9g

Sample collected	BG Final conc.	BG % removal	Breakpoint time (minutes)
1	0.001659	44.7	
2	0.001926	35.8	
3	0.002553	14.9	
4	0.002910	3.0	14
5	0.002916	2.8	
6	0.002925	2.5	