ADDIS ABABA UNIVERSITY

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School of Chemical and Bio Engineering

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"Decolorization of Cane Syrup by Activated Carbon Produced From Peanut Shell"

By

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A thesis submitted to School of Chemical and Bio-engineering, Addis Ababa institute of Technology, Addis Ababa University for partial fulfillment of Master of Science in chemical (process) Engineering.

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A Thesis submitted to the school of Chemical and Bio Engineering in partial fulfillment of the requirements of the Degree of Masters of Science in Chemical and Bio Engineering (Under Process engineering stream).

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Abstract

Sugar colourants are water soluble compounds present in sugar process products and the most impurities in sugar industry. Syrup decolorization can be achieved by sulphitation process. However, at the same time the formation of fine precipitate of $CaSO_4$ become difficult to eliminate trace of SO_2 in final sugar. The aims of this research were to produce activated carbon from peanut shell using KOH as an activating agent for syrup decolorization with lower color and lower residual sulfur dioxide levels and as an alternative waste management method. In this study, the first stage was producing granular activated carbon from peanut shell at different parameters such as: activation temperature (500^{o}C, 600^{o}C and 700^{o}C), KOH concentration (25, 50 and75%wt.) and particle size (0.5, 1.5 and 2.5mm). Low ash content (1.28%) with high percent of methylene blue adsorption (79.4%) of activated carbon was obtained having 0.5mm particle size, 0.26%wt. KOH, and 600^{o}C of activation temperature was with 0.965 desirability chosen as optimal activation parameter. The activated carbon at optimal condition was characterized in term of ultimate and proximate analysis, FT-IR and methylene blue adsorption efficiency. Using activated carbon, the effect of various process parameters like temperature, activated carbon dosage and time on decolorization of cane syrup was investigated. Under the experimental conditions of 45^{o}C, 1.4g activated carbon dosage for 75min was found to be the optimal condition for maximum cane syrup decolorization efficiency (75.5%). Consequently, the experimental results indicated that the peanut shell has a potential to be used as an activated carbon for decolorization of cane syrup.

Key words; peanut shell, activated carbon, cane syrup decolorization

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List of Abbreviations

AC	Activated Carbon
ADFs	Alkaline degradation products of fructose
ANOVA	Analysis of variance
BBD	Box-Behnken design
BET	Brunauer-Emmet-Teller
FTIR	Fourier-Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
MB	Methylene Blue
Ppm	Part of Per Million
Pzc	Point of zero charge
RSM	Response Surface Method

Chapter One

Introduction

1.1 Background

The development of color during sugar processing is a common problem for the sugar manufacturing industry. Juices and syrups produced as a result of processing contain compounds that end up in the sugar crystal. In sugar production, the production of white sugar consists of six steps; extraction, clarification, evaporation, crystallization, centrifugal separation and drying. The clarification step is aimed to decolorize the raw juice. The color of the finished product is the most important aspect.

The formations of colorants are produced by the nature of sugar cane and during factory processing. During factory processing colour formation is mainly due to sugar degradation reactions. Reducing sugars, such as glucose and fructose, formed by the inversion of sucrose, play an important role in the formation of color. These sugars degrade due to changes in operating conditions such as pH, retention time and temperature to form highly reactive intermediates, which undergo condensation and polymerization reactions to form highly colored polymers Riffer, R. (Ed.). (1988).

Sulfitation reduces the concentration of color compounds including plant pigments (phenolics and flavonoids), melanoidins and some color precursors such as organic acids and other decomposition products that can contribute to color development during later processing (Tanaka et al. 1972). Since sulphur has negative effect on human health, the evaluation of remaining sulphur in final sugar is the most important factor in its quality control based on international standard. The usage of sulphur should be limited because it causes to final sugar outside the standard.

According to the importance of the activated carbon and its use in the field of industry and pollution control, Physical, chemical, and surface characteristics of activated carbon determine its efficiency in removing the targeted sugar colorants. It is known as a material with a high content of carbonic and structure of follicular various, making it the active structure toward the adsorption of chemicals from their midst (Marsh, H., (2006). Activated carbon adsorbents having a large internal surface area and relatively nonpolar surface are primarily being used to remove organic compounds from both liquid and gaseous streams (Smisek and Cerny, 1970).

Nowadays, there is a great interest in finding inexpensive and effective alternatives to the existing commercial activated carbon. Exploring effective and low-cost activated carbon may contribute to environmental sustainability and offer benefits for future commercial applications. The cost of activated carbon prepared from biomaterials is very low compared to the cost of commercial activated carbon (Arulkumar M, Sathishkumar P, Palvannan T (2011)).

Activated carbons can be produced from virtually any type of carbonaceous materials such as coconut shell, palm shell, nut shell, olive stones, oil-palm stones, agricultural wastes, and many others. (Zhang et al, 2007). The peanut shells are a carbonaceous, fibrous solid of the mature pods contains chemical composition cellulose, carbohydrate, protein, minerals and lipids (Reddy, 1988 in Nautiyal, 2002). It contains 45% cellulose and 33% lignin as well as 1% fat, 7% protein, 4% ash and 10% moisture. The high content of cellulose and lignin should make peanut hulls a good candidate for cation adsorption (Albrecht, W. J. Peanut Hulls, 1979). Therefore, it is interested to prepare a higher value product such as activated carbon from peanut.

1.2 Problem Statement

Clarified juice is normally concentrated in evaporators and concentration increases from 15º brix to 65º brix which is known as syrup. In this stage colourants are formed due to brix increases. Also, Maillard reactions can occur with formation of melanoidins (Paton and McCowage, 1987). They are only produced with the application of heat at high brix and low purity, but can also form with low heat over long periods. The presence of melanoidins during boiling increases viscosity of syrups and become difficult for crystallization process (Kort, 1978). When a higher quality sugar is required, the benefits of syrup clarification are widely realized. Steindl and Doherty 2005, suggests that the effect of syrup clarification on sugar quality is generally greater than the improvements measured in syrup quality because high molecular mass impurities are removed. It can remove about 82 % of the turbidity, gives a small ash and colour improvement and reduces massecuite viscosity.

In Metahara sugar factory Decolorization process has been accomplished by following double sulphitation. At the stage of syrup sulphitation the SO_2 is used as a bleaching agent for lowering the color of syrup, but at the same time the formation of fine precipitate of $CaSO_4$ caused by the difficulties in eliminating trace SO_2 in the final product. Because of this sulphited salt, the factory is seeking to improve sugar quality and reduce residual sulfur dioxide levels and also it becomes difficult to sell produced sugar to beverage industries on the domestic and international market. Since sulfur has negative effect on final product quality, the color removal by activated carbon is the preferable to produce higher quality white sugar with lower color and lower residual sulfur dioxide levels.

According to cleaner production concepts Bonilla et al, (2010) suggests that the replacing granular activated carbon (GAC) derived from byproducts produced a lot of benefits for the environmental aspects, such as waste utilization and chemical reduction. Thus, this research is necessary to use agricultural waste peanut shell as a precursor to produce granular activated carbon (GAC) for syrup decolorization.

1.3 Objective

1.3.1 General objective

The main objective of this study was decolorization of cane syrup by activated carbon produced from peanut shell.

1.3.2 Specific objective

- ✓ To synthesize and investigate the effect of parameters such as activation temperature, particle size and KOH concentration on granular activated carbon production
- ✓ To select the optimum conditions in making activated carbon with low ash content and methyl blue adsorption
- ✓ To characterize the chemical and physical properties of granular activated carbon
- ✓ To determine the decolorization efficiency of granular activated carbon for cane syrup decolorization
- ✓ To investigate the effect of decolorization process parameters such as adsorbent dosage, contact time and bleaching temperature and to select the optimum conditions in cane syrup decolorization efficiency

1.4 Significant of study

The replacing AC derived from peanut shell produced a lot of benefits for the environmental aspects, such as waste utilization and give a solution towards final product quality by using low cost adsorbents to make safe environment.

In general, activated carbon production from agricultural waste like peanut shell has a lot of benefits such as:

- ✓ Produce adsorbent from low cost material which is available locally.
- ✓ give a solution towards final product quality by using low cost adsorbents to make safe environment
- ✓ provide useful knowledge and understanding of the bleaching process of syrup by activated carbon
- ✓ minimize trace amount of Sulphur in final sugar
- ✓ make the industry competitive locally and internationally

1.5 Scope of the study

This study deals with production of granular activated carbon (GAC) and cane syrup decolorization. The first stage is the conversion of peanut shell by-products to activated carbon by using different parameters; select the optimum condition based on quality of adsorbent and characterized the produced GAC by physical and chemical properties of the carbon. Finally, by taking factors that can affect decolorization process, investigate optimum parameter for better cane syrup decolorization efficiency.

Chapter Two

Literature Review

The goal of any production process is to produce as large a quantity of product within large quality criteria. One of the most important criteria in sugar production is color. Sugar colourants are water-soluble compounds present in sugar process products that absorb light in the visible spectrum. Due to different physical and chemical conditions during processing, colourants can be formed, removed or changed chemically.

2.1. Colorants in Cane Sugar

Sugar colorants are not one single molecular species, but it consists of a wide range of materials each with its own molecular weight, pH sensitivity, charge and chemical structure (Godshell & Baunsgaard, 2009). Colorants are named from their origin and mechanism of formation.

(Bento at al., Godshall et al) have been conducted colorants in cane sugar originate from two main sources: the sugarcane and the sugar refining process. The phenolic and flavonoids come from the nature of cane, where they exist as glycosides attached to sugar residues and from factory process. Each cane sugar colorant is placed into one of four descriptive groups: phenolic and flavonoids, caramels, melanoidins and alkaline degradation products of sucrose. In addition to these four groups, there are also colors precursors that do not themselves exhibit color but will react with another non-colored compound to form a colored compound under favorable reaction conditions.

2.1.1. Phenolic and Flavonoids

The phenolics and flavonoids come from the cane, where they exist as glycosides attached to sugar residues (Clarke et al., 1984). Smith and Gregory (1971) found that approximately two-thirds of the color in raw sugar comes from the phenolic and flavonoid group. Some phenolic are not colored when they first come from the plant, but oxidize, complex, or react to form colorants during processing. Phenolic compounds present a high IV and are involved in enzymatic and non-enzymatic browning reactions and in reactions with iron, forming very dark compounds.

2.1.2. Melanoidins

Melanoidins by definition are the colored end products of the Maillard reaction between an amine (e.g., amino acid) and a carbonyl compound (e.g., reducing sugar). Also known as the non-enzymatic browning reaction, the reaction mechanisms are complex, consisting of repetitive condensation, dehydration and polymerization reactions resulting in dark brown colored substances (Rizzi, 1997). They are only produced with the application of heat at high brix and low purity, but can also form with low heat over long periods. They are slightly negatively charged at neutral pH, but positive under acidic conditions. A sub-division of melanoidins is melanins, produced from phenol-amine reactions. These have a medium MW (> 2500) and are difficult to remove in processing. Melanoidins are insensitive to pH and hence have low indicator values (IVs).

The presence of impurities as iron, copper and phosphates can catalyze the reaction Formation of melanoidins take place mainly over 65° brix. As the brix increases, the contribution of Maillard products to solution colour increases (Paton and McCowage, 1987).

2.1.2.1 Factors that affect Melanoidin Formation

Reaction conditions play an important role in the fundemental structure of melanoidins. The composition of melanoidins depends temperature, heating time, pH, chemical composition of food system and water content during processing or storage of foods (Morales and Boekel, 1999).

- ✓ **Temperature**

The rate of melanoidin formation increases with temperature (Coca et al., 2004). It has been reported that, the effect of temperature on kinetic constants of non-enzymatic browning reaction in apple puree was described by Arrenhenius-type equation and the value of kinetic constant increased with temperature (Carabasa-Gibiret and Ibaraz-Ribas, 2000) and thus increase caused a faster darkening of samples. It has has also been verified by other authors that browning rate followed an Arrenhenius type of dependence upon temperature (Bostan and Boyacıoğlu, 1997); Buedo et al, 2001).

- ✓ **Time**

Several workers have derived theoretical equations to predict the extent of brown pigment as a function of time but they cannot be solved because of some variables, rate constants of intermediary reactions, are still unknown (Morales and Boekel, 1999) however it is explained by some others that the rate of melanoidin formation increases in proportion to the square length of heating at a given temperature (Mauron, 1981; Coca et al, 2004).

- ✓ **pH**

The pH has a significant effect on the Maillard reaction. In general, the rate and extent of browning increases with increasing pH (Kearsly and Dziedzic, 1984). The reaction generally has a minimum is at pH 3 (Lea and Hannan, 1949). At a pH < 3 and > 9, other nonenzymic interactions (i.e. sugar-sugar and protein-protein) compete with the Maillard reaction (Coca et al, 2004). The effect of pH is due to increasing pH increases the reactivity of aminoacids due to acid base equilibrium (Bostan and Boyacıoğlu, 1997).

2.1.3. Caramel

Caramels are produced by the polymerisation of thermally degraded products of sucrose at high temperatures (Baunsgaard et al., 2001). The products contain mixtures of oligosaccharides, polysaccharides and colored matter (Lindeman and O'Shea, 2001). These colloidal compounds formed have a tendency to remain on the outer surface of the sugar crystals, which affect the quality of the final raw sugar product it is the most difficult to remove and most often found in refined sugar. Under the harsh operating conditions in sugar factories (e.g., elevated temperatures, acidic pH), caramelisation takes place. The chemistry of caramelisation is poorly understood due to the complexity of the reactions taken place (Riffer, R. (Ed.). (1988)).

For caramels formation, sugar temperature must be higher than their melting point (185ºC) (Ahari and Genetolle, 1961). Although process temperatures are in average much lower than this, it can happen that sugar be accidentally in contact with temperatures higher enough to produce caramelization. Also, some impurity traces can catalyze caramels formation (Riffer, 1988).

2.1.4. Alkaline degradation products of fructose (ADFs)

Alkaline degradation products of hexose sugars are colored products formed as a result of the thermal decomposition of reducing sugars. The end products mainly consist of carboxylic acids, carbonyl compounds and lower molecular weight (LMW) polymers, which can lead to inversion of sucrose and further color formation. The degradation rate and composition are heavily dependent on temperature, juice pH and the presence of divalent actions (Coca et al., 2004). These compounds polymerize forming colourants with molecular weight between 1,000 and 5,000 Da (Parker, William, 1968).

2.1.5. Color precursors

These are compounds which, while not colored themselves, undergo reactions that form color during processing. They include amino acids, simple phenolic compounds, and 5-hydroxy- 2-methyl furfural (HMF), the last being formed from acidic decomposition of fructose (Mohamed Ahmedna,(2000).

Table 2.1: Main colourants formed in each step of the process

	production	extraction	clarification	evaporation	Sugar house
products	cane	Juice	juice	syrup	Syrup Massecuites Molasses Sugars
brix		Low	low	Low/high	High
Alkalinity		Low	High	Medium	Medium
Temperature		Medium	high	high	medium
colurants	CWP Flavonoids Phenolic acids	Enz.Brow.P.Phenols -Iron	HADP	Melanoidins Non Enz.BP caramels	Melanoidins Non Enz.BP Caramels

Source: Paton and P. Smith, 1983

2.1.6 Sugar colourants molecular distribution

According to (Godshall, 2008), the MW distribution, colourants are usually divided in the following groups: Low MW (LMW), Medium MW (MMW), High MW (HMW) and Very High MW (VHMW).

Low MW colourants, with MW lower than 2,500 Da include flavonoids, phenolic acids and other monomeric phenols. This group includes also products of the reaction of polyphenols with iron.

Medium MW colourants are those with MW ranging from 2,500 to 12,000 Da, as HADP (Hexoses Alkaline Degradation Products) and caramels.

High MW colourants, with MW ranging from 12,000 to 50,000 Da, include melanoidins and products of browning reactions involving phenols. This group of colurants has dark brown colour.

Very High MW colourants, with MW over 200,000 Da and passing through 0.45 _m membrane filter, comprise polysaccharides bonded to phenols or their oxidized products. Lindeman, 2001, refers that VHMW colourants have a high carbonyl character indicating a possible association with polysaccharides.

Table 2.2: Molecular weight of sugar colorant

Group	VHMW	HMW	MMW	LMW
MW	>200,000Da	12,000-50,000Da	2,500-12,000Da	<2,500Da
	Enzymatic BP of CWP	melanoidins	HADP	Flavonoids
		Phenols brow .prod	HMF Poiymers	Phenolic Acide
			Caramels	Phenols-Iron

Sourse: Godshall, 2005

2.2. Methods of decolorization

2.2.1. Sulfitation

Sulfitation is the practice of adding sulfur dioxide (SO_2), a bleaching gas, to cane juice and/or syrup for the purpose of color control. In many parts of the world, particularly developing countries, sulfur dioxide is used to process cane juice into a semi-refined white sugar. The advantage of using SO_2 is a much lower color in the produced sugar. Disadvantages include increased scaling problems in the evaporators, high sulfite content in the final product, higher sugar loss due to lower pH, and secondary color formation (color return) on storage (Ziegler, 1 1973).

2.2.2. Carbonation

Bennett (1972) performed extensive experiments on carbonation and phosphatation in the laboratory, coupled with X-ray diffraction (XRD) studies, to determine the mechanisms of color removal. He showed that the impurities are trapped within the growing calcium carbonate crystals, often distorting the crystals, rather than being adsorbed onto the surface after precipitation. Any kind of color body that has some acidic (anionic) character and is capable of forming a weak linkage with calcium (i.e. a sparingly soluble calcium salt) will get incorporated into the precipitate. Clarke et al (1985) found that carbonation generally removed more phenolics and amine colorants than did phosphitation, although it was also stated that phenolic can be formed during carbonation.

2.2.3. Phosphitation

Phosphatation-flotation is a widely practiced method for the defecation of a raw sugar melt. The process involves the coagulation of impurities with a calcium phosphate precipitate followed by the flotation of this coagulum to yield a clear liquor underflow. A thorough review of the phosphatation process was done by Saranin (1972), and this work should be consulted for further details on operation of the process. Saranin concluded that the tricalcium phosphate precipitate occludes and absorbs fine colloidal solids and soluble color. Most colloids in sugar liquors have negative charges, and so the addition of a cation such as calcium neutralises these charges and allows flocculation to take place. Accordingly, the anionic color bodies are most effectively removed by this process, and some soluble colors are absorbed by the precipitate. But Bardwell et al (1985) found that the process had a lower capacity for flavonoids than had other processes and it is costy.

2.2.4. Ion exchange

Ion exchange resin is normally used for sugar decolorization and it is regenerated by washing with saline water. Therefore, treatment, and disposal of the saline water are major production issues. Activated carbon (AC) can be produced from carbon sources such as coal (Ahmadpour and Do, 1996; Teng et al., 1996; Punsuwan, 2002).

Table 2.3: Effect of decolorization process effect on color type

COLOR PROCESS	Phenolic	Flavonoids	Melanoidins	Caramels	ADF Products	Color Precursors
Carbonatation	Okay	X	Okay	Okay		
Sulphitation	Okay	Okay	Okay			Okay
Phosphatation	X	X	Okay	Okay	Okay	
Color Precipitant			Okay	Okay	Okay	
Oxidative Decolourants	Okay	Okay				Okay
Ion Exchange	X	X	Okay	X	Okay	
Activated Carbon	Okay	Okay	Okay	Okay		Okay

Source: Davis S S.B., 2001

2.2.5. Activated carbon

Activated carbon is a black solid substance resembling granular or powdered charcoal. It is a processed carbon material with a highly developed porous structure and a large internal specific surface area. Activated carbon (AC) is a well-known adsorbent that can be used efficiently for removal of a broad spectrum of pollutants from air, soil and liquids. Adsorbents are usually porous solids, and adsorption occurs mainly on the pore walls inside particles (Hassler, J. W 1974).

Activated carbons (ACs) can be produced from any carbonaceous materials, both naturally occurring and synthetic. Process economics however dictates the selection of readily available and cheaper feed stocks. Most commonly used precursors for the production of commercial ACs are coconut shell, wood, fruit stones, etc. Biomass precursors offer most economical service because they are renewable with low mineral content and appreciable hardness.

Typically, all organic precursors can be converted into activated carbons; however, in most cases, it requires the usage of an activation agent and only a few are commercially attractive. The properties of the final product depend on the nature of raw material used, the nature of activating agent, and the conditions of activation process (R.C. Bansal et al, 1998). The high adsorptive capacity of Activated carbon is associated with its internal porosity and other properties such as surface area, pore volume and pore size distribution (C.P Huang,et al 1980). These properties have been determined not only by the physical properties and the chemical composition of the precursor, but also by the activation process of lignocellulosic precursors (A. Bota,et al 1997).

2.2.5.1 Pore structure

The word pore comes from the Greek word, meaning a passage (Marsh, 1989). In this sense, a pore is a class of void which is connected to the external surface of a solid and will allow the passage of fluids into, out of, or through a material. Marsh's (1989) claim that, in the scientific literature on porous solids the terms 'open pore' and 'closed pore' are used, the former a pore which is not so connected.

Activated carbons have a number of unique characteristics such as large internal surface area, chemical properties and good accessibility of internal pores. Differences in pore sizes affect the capacity for molecules of different shapes and sizes, and this is one of the criteria by which carbons are selected for a specific application. Porosity is classified by IUPAC into three different groups of pore sizes
(Guo and Lua, 2003):

- ✓ Macropores (above 50nm diameter)
- ✓ Mesopores (2-50 nm diameter)
- ✓ Micropores (Under 2 nm diameter)

Micropores generally contribute to a major part of the internal surface area. Macro and micropores can generally be regarded as the highways into the carbon particle, and are crucial for kinetics. The desired pore structure of an activated carbon product is attained by combining the right raw material and suitable activation procedure.

The schematic of internal pores structure in activated carbon was shown in Figure 2.1 below.

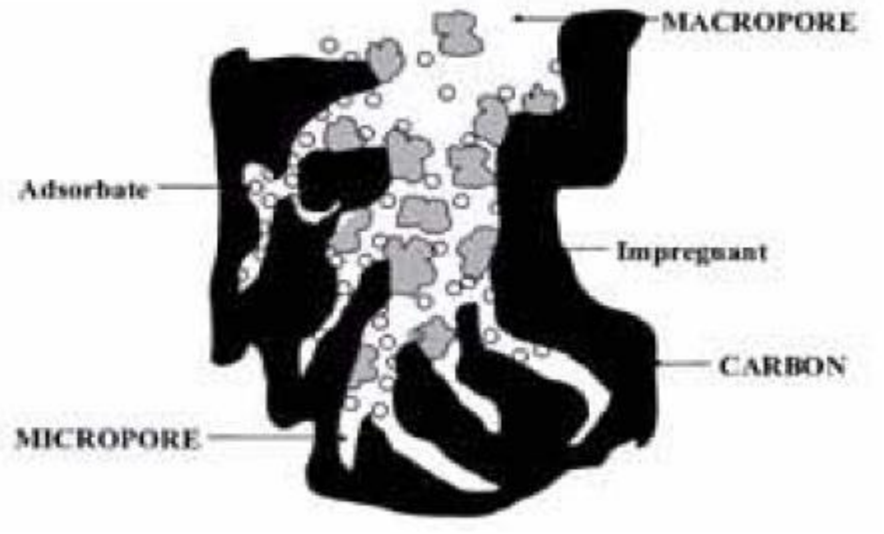


Fig 2.1: The schematic of internal pore structure in activated carbon

The pore size distribution also affects the efficiency and selectivity of adsorption. A consideration of the dimensions of some pollutants shows that activated carbon can feasibly be used to remove many of the impurities occurring in water (Radovic, 2001). The small organic molecules with low solubility have sizes in the range 0.6 to 0.8 nm and can be adsorbed in micropores while large compounds such as color molecules and humid acids have dimensions around 1.5 to 3.0 nm that will favor their adsorption in mesopores..

2.3. Production of Activated Carbon

Activated carbon can be prepared from various raw materials including agricultural and forestry residues. Generally, most of the precursors used for the preparation of activated carbon are rich in carbon (Prahas et al., 2008). Production of AC was achieved typically through two routes, physical activation and chemical activation (Bansal et al., 1998).

Physical activation involves carbonization of raw material followed by the activation at high temperatures (between 800 and 1100 ^{o}C) in the presence of oxidizing gases like carbon dioxide or steam (Aworn et al., 2009). Whereas chemical activation mixing of chemical agent with precursor and then followed by pyrolysis at moderate temperatures in the absence of air (Ahmadpour and Do, 1997).

2.3.1. Physical Activation

Physical activation is a two-step process. It involves carbonization of raw material followed by activation at elevated temperatures in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures. Carbonization temperature ranges between 400^{o}C to 800^{o}C, and activation temperature ranges between 800^{o}C to 1100^{o}C.

A) Carbonization

The main purpose of carbonization is to reduce the volatile content of source material in order to convert it to a suitable form of activation. During carbonization process cellulose and lignin (in the case of lingo cellulosic carbon precursors) are transformed into condensed aromatic systems (L. S. Singer, 1961). During the phase of carbonization, by the pyrolytic decomposition of the precursor in the presence of an inert gas such as nitrogen, most of the non-carbon elements, particularly oxygen, nitrogen, and sulfur, are removed. The pyrolyzed product or char, with a poorly developed structure, consists of more or less disordered elementary graphitic crystallites. As a result of deposition and decomposition of tarry substances, free interstices between these crystals are filled or at least blocked by disorganized (amorphous) carbon. (Smisek and Cerny, 1970, 1992).

B) Steam or CO_2 Activation

Second step of physical activation is high temperature gasification (activation) using oxidizing agents such as steam or carbon dioxide (CO2), which produces activated carbon with high porosity (Mantell, C. L. (1946)). Porosity development is due to the penetration of oxidizing agent into the internal structure of char and removal of carbon atoms by reaction which results in opening and widening of inaccessible pores (Marsh, H., (2006)). Subsequent activation is required to increase surface area and create a highly developed pore structure for the selective adsorption of molecules of different sizes and polarities.

2.3.2. Chemical Activation

Preparation of activated carbon by chemical activation is a single step process in which carbonization and activation is carried out simultaneously. Chemical activation is usually carried out by impregnating the raw or pre-carbonized material with an activating agent, which acts as dehydrating agent and oxidant and pyrolyzed between 400 and 800 C in the absence of oxygen. The most commonly used activating agents are phosphoric acid, hydrochloric acid, sulphuric acid, alkalis namely KOH and NaOH, zinc chloride and alkaline metal compounds (L. Wang, W. R. Zhao, and Z. B. Wu, 2007). The resultant activated carbon is washed, dried till constant weight is obtained and ground to required size. Activated carbons produced by chemical activation generally exhibit a very open structure and bottle shaped, ideal for the adsorption of large molecules.

2.3.2.1. Advantages of chemical activation over physical activation

Chemical activation offers several advantages over physical activation which mainly include that the process normally takes place at a lower temperature and for a shorter time (< 800 ^{o}C) than those used in physical activation (800 – 1100 ^{o}C). In addition, very high surface area activated carbons can be obtained with the yields of carbon in chemical activation being usually higher than those in physical activation because the chemical agents used are substances with dehydrogenation properties that inhibit the formation of tar and reduce the production of other volatile products (Bansal et al 1988).

2.4 Classification of Activated Carbon

Activated carbons are complex products and the classification is difficult based on their preparation methods, physical properties, and surface characteristics. However, the general classification of activated carbons based on particle size divides them into Powered Activated Carbon (PAC), Granular Activated Carbon (GAC), and Activated Carbon Fibres (ACF) (Babel and Kurniawan, 2004).

2.4.1 Powered Activated Carbon

Powered Activated Carbon (PAC), has a typical particle size of less than 0.1 mm and the common size of the particle ranges from 0.015 to 0.025 mm. Typical applications of PAC are industrial and municipal waste water treatments, sugar decolorization, in food industry, pharmaceutical, and mercury and dioxin removal from a flue gas stream (Cook et al., 2001).

2.4.2 Granular Activated Carbon

Granular Activated Carbon (GAC), has mean particle size between 0.4 to 4 mm. It is usually used in continuous processes of both liquid and gas phase applications. GAC has an advantage over PAC, of offering a lower pressure drop along with the fact that it can be regenerated and therefore reused more than once. In addition to the proper micropore size distribution, its high apparent density, high hardness, and a low abrasion index made GAC more suitable over PAC for various applications (Cerminara et al., 1995).

2.5 Factors Affecting Activated Carbon Production

2.5.1 Raw materials

Raw material will have an impact on the properties of activated carbon produced as activation: Pore structure and Purity of the end product. Since an activated carbon is structurally a non-graphitic carbonaceous material, almost any carbonaceous solid material and low inorganic mater can be converted into activated carbon (F. Rodriguez-Reinoso, 1997). There are previous studies relating to this, AC with high surface area and pore volume can be produced from a large number of carbonaceous raw materials like agricultural waste which include rice husk, coal, cane bagasse, peanut shell and other by-products due to low cost of production scraps (Kirk- Othmer , 1964).

Most organic materials rich in carbon that do not fuse upon carbonization can be used as raw material for the manufacture of AC (Rodriguez-Reinoso,2002). The selection of raw material for preparation of porous carbon, several factors are taken into consideration.

The factors are:

- ✓ High carbon content
- ✓ Low in inorganic content (i.e low ash)
- ✓ High density and sufficient volatile content
- ✓ The stability of supply in the countries
- ✓ Potential extent of activation
- ✓ Inexpensive material
- ✓ Low degradation upon storage

In general, the three main structural components of stems of plant are hemicellulose, cellulose and lignin. Among several structural components of the plant, hemicelluloses are more sensitive to temperature and they are the first to decompose in the temperature range of 473 to 533 K during pyrolysis. Cellulose is thermally more stable than hemicellulose and will decompose in the range of 513 – 673 K releasing structural water. Lignin is the most thermally stable component. Decomposition of lignin takes place in the temperature range of 553 – 823 K resulting in the formation of large amount of aromatics (Rodriguez-Reinoso, 2002).

Raw material such as coconut shell and fruit stones are very popular for many types of AC, because their relatively high density, hardness and volatile content are ideal for manufacture of hard granular AC. Coconut shells, together with peach and olive stones are used commercially for the production of microporous activated carbons, useful for a very wide range of applications (Manocha, 2003).

The peanut shells are a carbonaceous, fibrous solid of the mature pods contains chemical composition cellulose, carbohydrate, protein, minerals and lipids (Reddy, 1988 in Nautiyal, 2002). It contains 45% cellulose and 33% lignin as well as 1% fat, 7% protein, 4% ash and 10% moisture. The high content of cellulose and lignin should make peanut hulls a good candidate for cation adsorption (Albrecht, W. J. Peanut Hulls, 1979).

AC should possess sufficient mechanical strength otherwise particle will be very unstable and readily crumbles and dust formation can Occur due to the continuous mechanical friction between carbon particle and sugar liquor and also it slows down the filtration rate and decreases the amount of regenerated carbon. Peanut shells contain cellulose, hemicelluloses, and lignin (G.U.Raju, S. Kumarappa and V.N. Gaitonde, 2012). Therefore, peanut shell is selected as a raw material for this study because of inexpensive material with high carbon content, low inorganic content, low ash content and a hard cover.

2.5.2 Temperature

Temperature, particularly the final activation temperature, affects the characteristic of the activated carbon produced. Generally, for commercial activated carbon usually conducted at temperature above 800°C in a mixture of steam and CO_2 (San Miguel, et al.,2003). Recently, the researchers have been working out on optimizing the final activation temperature to economize the cost of production and time. As reported by several authors, activation temperature significantly affects the production yield of activated carbon and also the surface area of activated carbon. The temperature used as low as 200°C (Haimour and Emeish, 2005) and up high to 1100°C (San Miguel, et al.,2003).

The increasing of activation temperature reduces the yield of the activated carbon continuously. According to Guo and Lua(2003), this is expected since an increasing amount of volatiles is released at increasing temperature from 500°C to 900°C. The decreasing trend in yield is paralleled by the increasing activation temperature due to the activation reaction. These phenomena are also manifested in the decreasing volatile content and increasing fixed carbon for increasing activation temperature.

Previously, Haimour and Emeish(2005) suggested that the percentage of volatile matter decreased with an increase of carbonization temperature and the variation of this parameter was maximum between 200°C and 800°C due to rapid carbonization occurring in this region. It is also unsuitable to prepare activated carbon when carbonization temperature was more than 800°C since the successive decreased in volatile matter is minimal above this range. This was accompanied with an increase of fixed carbon and ash content which may be attributed to the removal of volatile matter in the material during carbonization process. Thus, leaving behind the more stable carbon ash-forming minerals also increase (Haimour and Emeish, 2005).

2.5.3 Activation time

Besides activation temperature, the activation time also affects the carbonization process and properties of activated carbon. From previous study, the activation times normally used were from 1 hour to 3 hour for palm shell and coconut shell (Srinivasakannan and Zailani, 2003). As the time increased, the percentage of yield decreased gradually and the BET surface area also increased. This result is possibly due to the volatilization of organic materials from raw material, which results in formation of activated carbon. The extent of decrease in product yield is observed to be reducing when excessive activation occurs (Kim et al., 2001).

2.5.4. Activation reagent

During chemical treatment, chemical agents such as alkaline chemicals (KOH, NaOH, Na_2CO_3 and $NaHCO_3$), acid chemicals (HCl, H_2SO_4 and $C_2H_4O_2$) and other chemicals ($ZnCl_2$ etc) are added with purpose of improving the surface area or size of porous structure in AC materials. Girgis et al (2007) produced activated carbon from oil palm stones using all three agents and activated at 500 and 650^{o}C. He reported that zinc chloride and phosphoric acid activation yielded essentially micro porous network whereas the use of potassium hydroxide gave well developed meso porous activated carbon.

According to Wigmans (1989), Carbons with a large percentage of micro pore volume or surface area were poor adsorbers of sugar colorants. An activated carbon with a high percentage of micro pores will tend to adsorb low molecular weight compounds and as the percentage of micro pores decreases, the carbon can adsorb compounds with a broader range of molecular sizes and meso porous activated carbon is best for sugar decolorization.

2.6. Properties of activated carbon for use in sugar Decolorization

Characterization for activated carbon (AC) is very important in order to classified AC for specific uses. Basically, AC characterized by physical properties and chemical properties. As Guo and Lua(2003) mentioned that the characteristics of activated carbon depends on the physical and chemical properties of the raw materials as well as activation method used. Physical, chemical, and surface characteristics of activated carbon determine its efficiency in removing the targeted sugar colorants.

Physical properties of AC, such as ash content and moisture content can affect the use of a granular AC and render them either suitable or unsuitable for specific applications. While the specific surface area of activated carbon and surface chemistry is classified as chemical properties of activated carbon.

2.6.1. Physical properties

- ✓ **Moisture Content**

Activated carbon is generally priced on a moisture free basis, although occasionally some moisture content is stipulated, e.g., 3, 8, 10%. Unless packaged in airtight containers, some activated carbons when stored under humid conditions will adsorb considerable moisture over a period of month. They may adsorb as much as 25 to 30% moisture and still appear dry. For many purposes, this moisture content does not affect the adsorptive power, but obviously it dilutes the carbon. Therefore, an additional weight of moist carbon is needed to provide the required dry weight (Mantell, 1946).

- ✓ **Particle size**

The smaller the particles size of a porous carbon, the greater the rate of diffusion and adsorption. Intraparticle diffusion is reduced as the particle size decreases, because of the shorter mass transfer zone, causing a faster rate of color adsorption (Cookson, 1978). Powdered activated carbon mixes intimately with liquid, providing a higher contact area than granular activated carbon and, therefore, has better decolorizing power. However, very fine powdered carbon, that is, the fraction that can pass through a No. 80 sieve, is undesirable and is discarded as dust because these particles adversely affect filtration flow rate and promote channeling (Carpenter, 1985). This causes shorter filter cycles and increases carbon treatment cost. Therefore, carbon with proper particle size should form a good filter cake is essential to act as good filter aids and to reduce pressure drop during filtration.

- ✓ **Bulk density**

Density is particularly important in sugar decolorization. When two carbons differing in bulk density are used at the same weight per liter, the carbon having higher bulk density will be able to filter more liquor volume before the available cake space is filled. Carbons with an adequate density also help to improve the filtration rate by forming an even cake on the filter surface. Generally, a carbon with a bulk density of about 0.5 g/mL is adequate for sugar decolorization (Carpenter, 1985).

- ✓ **Hardness**

A carbon should possess sufficient mechanical strength to withstand the abrasion resulting from continued use. In the course of carbon usage, particle breakdown and dust formation occur due to the continuous mechanical friction between carbon particle and sugar liquor. Dust formed by attrition is undesirable because it slows down the filtration rate and decreases the amount of regenerated carbon. Therefore, carbons designed for sugar decolorization should have enough abrasion resistance to minimize attrition (Ahmedna, 2000a; Kirk-Othmer, 2001).

2.6.2. Chemical properties

- ✓ **PH value**

Activated carbon pH may influence color by changing the pH of the sugar solution. Such a change affects the pH-sensitive fraction of solution colorants, causing unreliable color measurements (Ahmedna et al., 1997a). Moreover, acid carbons, for example, may be a better decolorizer (Paton and Smith, 1983); but a sugar refiner would seldom employ a highly acidic carbon because the acid would cause inversion of sucrose to non crystallizable sugars, with subsequent lower yield (Mantell, 1946).

Bernardin (1985) reported that, in sugar decolorization, a distinctly acidic activated carbon may cause inversion of sucrose, and a distinctly alkaline carbon may cause color development through alkaline degradation of organic impurities. Hence, a carbon pH of 6-8 is acceptable for most applications.

- ✓ **Ash (minerals) content**

Ash content of carbon is the residue that remains when the carbonaceous portion is burned off. The ash consists mainly of minerals such as silica, aluminum, iron, magnesium, and calcium. Ash in activated carbon is not desirable and is considered an impurity. Ash leached into sugar liquor during the process of decolorization. Ash may also interfere with carbon adsorption through competitive adsorption and catalysis of adverse reactions. For instance, the ash content may affect the pH of the carbon since the pH of most commercial carbons is produced by their inorganic components (Ahmedna, 2000a).

- ✓ **Surface Chemistry**

The adsorption capacity of activated carbons is also strongly influenced by the presence of functional groups at the carbon surface. Activated carbons are known to contain a variety of heteroatoms such as oxygen, hydrogen, chlorine and sulfur. Heteroatoms are either derived from the starting material, and as a result of carbonization they become a part of chemical structure, or chemically bonded to the carbon during activation or during subsequent additional treatments, such as oxidation. These heteroatoms are bound to the edges of the carbon layers and form surface groups that greatly affect the adsorption behaviour of the activated carbon, with carbon-oxygen surface structures being by far the most important in influencing surface characteristics (Ahmedna, 2000a). The groups more frequently suggested to be present on the surface of activated carbon include; carboxyl groups, phenolic hydroxyl groups, normal lactones, carboxclic acid anhydrides and cylic peroxide. Carboxylic, lactone and phenolic are the functional groups generally considered as the ‘acidic surface oxides’ (Cheremisinoff and Ellerbusch, 1978).

2.5.3. Surface properties

- ✓ **Surface area**

Surface area is the single most important characteristic of activated carbon designed for adsorption of compounds from liquid media such as sugar liquor (Weber and Vliet, 1980).

Because of its large surface area (1 quart of Granules= 6 football fields of area), activated carbon has a great ability to adsorb organic and inorganic molecules from liquids or vapors (Roy, 1995). Large surface area is generally a requirement for a good adsorbent. For adsorption of compounds from liquid media such as sugar syrups, surface area is an important characteristic of an activated carbon. Since activated carbon has a large surface area due to having highest adsorptive porosity of any material known, it has a high capability of adsorbing organics such as colored materials from syrups. However, pore size distribution and surface chemistry should also be considered while selecting a good adsorbent. (Hutchins, 1997; Ahmedna, 2000a)

- ✓ **Pore size distribution**

The total porous structure of an activated carbon is formed by a wide range of pore sizes. For practical reasons, pore sizes are classified into three main types according to their width: macropores (> 50 nm), mesopores (2-50 nm), and micropores (< 2 nm). A carbon with substantial mesoporisity is generally recommended for adsorption of sugar colorants, which are made up of mixtures of compounds with varying molecular size (Ahmedna, 2000a). The presence of high microporosity would make adsorption of larger molecules, as found in sugar colorants, problematic. These large molecules would have difficulty entering and navigating through the micropores with the possibility that the micropores could become clogged, thereby effectively closing down further adsorption (B. Pendyal (1998).

Chapter Three

Materials and Methods

3.1 Raw Materials

3.1.1 Sample Collection and Pretreatment

Peanut shells used as precursors in this study were collected from Babile, which is located around Harar. The shells were washed with tap water to eliminate the impurities, dusts and water soluble substances, dried at 105 °C for 12hr prior to their activation. Then after, the dried sample was ground by using electrical grinder and sieve using USA test standard stainless steel sieves to obtain samples of 0.5mm, 1.5 & 2.5mm sieve size and used for the next experimental work. The proximate and elemental analysis results for raw materials had done.

3.2 Methods

3.2.1 Experimental setup

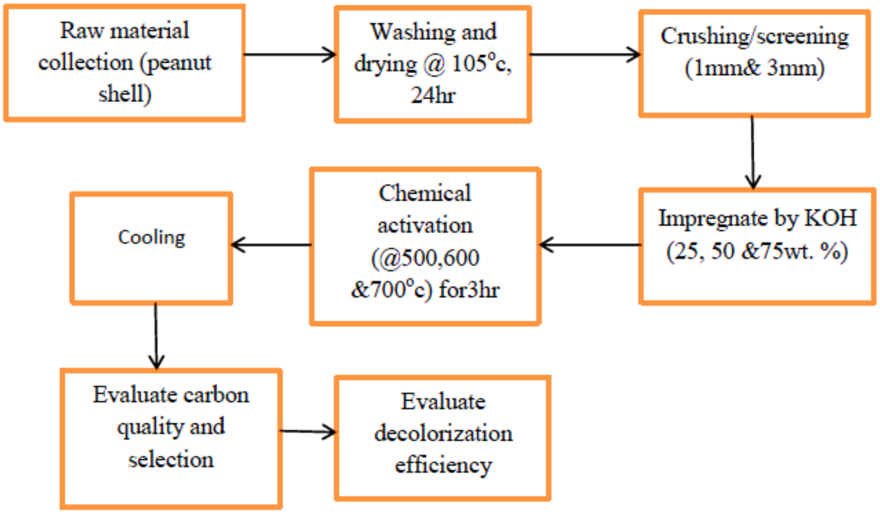


Fig. 3.1: Experimental Setup Flow Diagram

3.2.2 Activated Carbon Preparation

In this study, Chemical activation method for various conditions was used for the production of granular activated carbon by using potassium hydroxide (KOH) as activation reagent. This method can inhibit the formation of tar and reduce the production of other volatile products and thereby enhancing the yield of carbon with a better porous structure (Bansal et al 1988).

The prepared raw material was impregnated by KOH solution with different concentration (25wt.%, 50 wt. % & 75wt.%) in 1:1 (raw material/chemical) ratio and kept for overnight at the room temperature to ensure the access of activation agents to the interior of the precursor, to increase surface area and yield of carbon. After impregnation, the sample dried at 105^{o}c for 12 hrs.

Finally, the resulting samples were carbonized in a modified electric furnace at temperatures of 500, 600, and 700°C for durations of 120 minutes under nitrogen gas flow to purge the air inside the furnace before and during the activation process. The obtained carbon samples were kept in desiccator to cool. After cooling, the samples were washed with hot deionized water in order to remove salts and other impurities then rinsed several times with hot distilled water until the pH of the filtrate is becomes neutral. Finally, the obtained product was dried at 105°C for 12 hrs and stored in glass bottle for characterization and adsorption processes.

3.2.3 Characterization of the Prepared Activated Carbon

3.2.3.1 Determination of Moisture Content

Thermal drying method was used in the determination of moisture content of the activated carbon. About 1.0 g of the dried AC was weighed and placed in washed, dried and weighed crucible. The crucible was placed in an oven and dried at 105°C to constant weight for 4 hrs. The percentage moisture content was computed as follows:

$$\text{Moisture } (\%) = \frac{\text{Loss in weight on drying(g)}}{\text{initial sample weight(g)}} \times 100 \qquad (3.\ 1)$$

3.2.3.1 Volatile matter

The volatile matter, sometimes called volatiles consists mainly of the gases and water and tarry vapours evolved from coal when it is heated at high temperature. To determine it, Crucible is weighed empty (B).1 gm of AC is taken in a silica crucible with a porous silica cover and was weighed (C). The cover is used to avoid oxidation. The AC is then heated for 7 minutes at a constant temperature of 900°C inside a furnace. After heating the crucible is cooled and transferred to a desiccator. After few minutes the silica crucible is re-weighed (D) and the volatile matter content (VM) is determined in % according to equation 3.3, where E is weight loss in % and F is moisture content in % (ASTM, 2010).

$$E = \frac{(C-D)}{(C-B)} \times 100 \tag{3.2}$$

$$VM = E - F \tag{3.3}$$

3.2.3.2 Ash content

Ash in activated carbon is not desirable and is considered an impurity. Ash has bleached into sugar liquor during the process of decolorization process. The crucible was pre-heated in a muffler furnace to about 650ºC, cooled in a desiccator and weighed. About 1.0 g of CSAC was transferred into the crucibles and reweighed. The crucible containing the sample was then placed in a muffle furnace and the temperature was allowed to rise to 650ºC and burnt for 7 hrs in an electrical furnace. Finally, it was removed and allowed to cool in a desiccator to room temperature (30ºC) and reweighed again (S. Gueu, 2007).

The ash content was calculated using the equation (3.4)

$$\text{Ash}(\%) = \frac{\text{Ash Weight(g)}}{\text{Oven dry Weight(g)}} \times 100 \tag{3.4}$$

3.2.3.3 pH at the point of zero charge

The point of zero charge (pH_{PZC}) is defined as the pH of the mixtures at which surface charge density on the material is zero.

The $pH_{PZ}C$ value was determined by the solid addition method. The solutions (20 mL) with pH varying from 5.5 to 8.5 were transferred to a series of 100mL conical flasks. The pH values of each solution were adjusted by adding either 0.1N HCl or NaOH and were measured. One gram of activated carbon was added to each flask; the suspensions were then shaken by shaker incubator with a temperature of 25ºC. After twenty-hour agitation, final pH was measured. The results are plotted with pH final – pH initial against pH final. The point at which pH = 0 is known as pH_{ZPC} (Sreenivasa Rao et al 2011). High precision pH meter (Hanna, model HI11310) equipped with a combined glass electrode (Hanna) was used.

3.2.3.4 Bulk density

The bulk density is calculated as the ratio of the weight to its volume and expressed in g cm^{-3} (ECCMF, 1986).

$$\text{Bulk density} = \frac{\text{Weiht of dry sample(g)}}{\text{Volume of Packed dry material(cm3)}} \qquad (3.5)$$

3.2.3.5 Determination of Electrical Conductivity

High conductivity values indicated that an acid or water wash was not enough to reduce leach able ash to levels observed in commercial carbon.

To measure conductivity Suspensions of the samples (1% w/w) in distilled water subjected to continuous stirring for 20 minute, and the electrical conductivity of the solution was measured (Ahmedna et al., 1997b) at 25.6^{o}C using a conductivity-meter.

3.2.3.6 Infrard spectroscopy analysis

FT-IR spectroscopy was used to identify the chemical groups present in the raw material and ACs.The electronic structure of carbon samples were examined using FT-IR 1725 x (perkin-Elmer) spectrometer. The measurements were carried out over the range 4000-400cm-1.

3.2.3.7 Methylene blue number

The adsorption characteristics are denoted as the quality control parameters for any activated carbon. Quality control parameters are expressed in terms of methylene blue number. Batch adsorption experiments were conducted in order to determine the maximum adsorption capacity of adsorbent. To measure this, first the methyl blue solution with different concentration (1-15mg/L) in 100ml Erlenmeyer flasks. Then, the absorbance of the dye solution was measured by using UV-spectroscopy and prepares an absorbance versus concentration standard curve of MB. After the standard curve was prepared, 0.1g of activated carbon from each sample added to 5mg/l methylene blue solution for 1hr. After separation the absorbance of filtrate also measured by using spectro-photometer at 620 nm.

The removal efficiency of the prepared activated carbons was calculated using the given formula as follow:

$$\%\text{MB removal} = \frac{\text{Co} - \text{C1}}{\text{Co}} \times 100 \qquad (3.6)$$

Where:

Co: is initial concentration of methylene blue before adsorption

C1: is remaining concentration of methylene blue after adsorption

3.2.3.8 Elemental Analysis

Elemental analysis was carried out using CHNS/O analyzer to determine the polarity of activated carbon.

3.2.3.9 The activated carbon pH measurement

Determination of pH was performed by gently boiling to $90^{o}C$, subjected to continuous stirring for 20 minute, cooled to room temperature and the pH of the solution was determined using a pH-meter in order to determine basic, acid or neutral nature (Ahmedna et al., 1997b). The Buffer solution with a pH 4.0, 7.0 &9.0 was used as a reference.

3.3 Decolorization process

Batch adsorption experiments for adsorption of colorants on cane syrup were conducted by using prepared activated carbon. For each run, a definite amount of GAC was added to 100 ml syrup. All the adsorption experiments were carried out at constant shaking speed of 125 rpm agitator. Adsorption of colourants on developed GACs was conducted with 100 ml of syrup taken into 250 ml Erlenmeyer flasks by varying different parameters such as adsorbent dosage, bleaching temperature and contact time. / 100ml) and contact time (30, 45 & 60min).

The effect of contact time on batch adsorption of colour removal of syrup with a variation of contact time ranged from 30, 45 and 60 min was studied by agitating in 100 ml of syrup solutions at 60^{o} brix. Whereas, the effect of various amounts of AC also studied by varying the weight of AC (1, 2 & 3g) without changing the volume of syrup solutions, (100 ml) with constant speed of 125 rpm.

The adsorption tests were carried out in batch system by adding various amounts of activated carbon in 100ml syrup solution with time variation at 60 ^{o} brix. Color was parameters to evaluate decolorization efficiency.

3.3.1 Cane Syrup Analysis

- ✓ **pH Analysis**

The pH of sugar syrup was determined by simply reading of pH meter which is standardized by buffer solutions of PH 4, 7 & 9.

- **Turbidity Determination**

The turbidity of clarified juice is a measure of the effectiveness of the clarification process. The ICUMSA Colors of Unfiltered and filtered samples were measure at 420nm and the difference between the readings is the turbidity of the sample. NaOH and HCl also used as reagent.

- **Decolorization Efficiency**

The extent of colour removal was investigated separately by changing adsorption dose, contact time and syrup temperature. After adsorption, the adsorbent was separated from the solutions using vacuum filter. And after adsorption, the absorbance was determined by UV–spectrophotometer. Before decolorization, the absorbance of cane syrup was determined using spectrophotometer at 420 nm against water using a 10 mm cell, measure of the color, and the color level was expressed in ICUMSA units. At the end of adsorption time, the decolorized syrup was filtered using filter paper to completely remove the activated carbon, and the color was measured again.

$$\text{Color(IU)} = \frac{10^8 * A}{b * c} \qquad (3.7)$$

Where A = absorbance at wavelength 420 nm.

b = length of the absorbant path (cm)

c = concentration of sample (g/ml)

$$\text{Decolorization efficiency} = \frac{\text{IUinitial} - \text{IUfinal}}{\text{IUinitial}} \times 100 \qquad (3.8)$$

3.3 Design of experiment

In this study, Process optimization of the experimental conditions were carried out following a standard Design-Expert 7.0.0 software Box-Behnken design (BBD) of response surface methodology (RSM). This design of the experiment helps us to optimize and set combination of process parameters with a minimum number of experiments, as well as to analyze the interaction effect between those parameters. RSM designs allow us to estimate interaction; even the quadratic effects and gives us an idea of the shape of the response surface.

A Box-Behnken design (BBD) was used in the optimization of process variables with three factors at three levels with 17 runs, including 5 central points to evaluate the effects of three independent variables (particle size, activation temperature & KOH concentration) on the ash content & methylene blue decolorization efficiency of activated carbon and also (carbon dosage, time& bleaching temperature) on color removal of cane syrup. The responses function was partitioned into linear, quadratic, and interactive components. The model adequacies were checked in terms of the values of R^2 and adjusted R^2. Analysis of variance (ANOVA) was employed to determine the significance of the models. Verification of optimized conditions and predicted values were done in duplicate to confirm the validity of the models.

Table3.1 Experimental factors and levels for AC preparation and decolorization efficiency

Stage I (AC Preparation)						**Stage II (Decolorization Efficiency)**				
Variables	**Unit**	**Levels**				**Variables**	**Unit**	**levels**		
		-1	**0**	**1**				**-1**	**0**	**1**
Particle Size	mm	0.5	1.5	3		**Contact time**	min	30	45	60
Activation Temperature	^oC	500	600	700		**Carbon dosage**	g/100ml	1	2	3
KOH	Wt.%	25	50	75		**Syrup Temperature**	^oC	30	45	60

According to BBD the total number of experiment can be calculated as:

$$N = K2 + K + Cp$$

Where k is a number of factors, and C_p is a central replication point

Based on this formula a Box-Behnken design (BBD) was used in the optimization of process variables with three factors at three levels with 17 runs, including 5 central points to evaluate the effects of three independent variables

Chapter Four

Result and Discussion

4.1. Raw Material Characterization

Quality of activated carbons not only depends on the experimental conditions of the carbonization and activation steps but also preponderantly on the original nature and structure of the involved material.

Proximate analysis and ultimate analysis have been used for the determination of characteristics of carbonaceous materials that may be used as precursors for activated carbons. For this specific study proximate composition analysis and ultimate analysis was done was done at laboratory & at 4 kilo campus.

4.2.1 Proximate analysis

The proximate analysis of peanut shell includes the determination of moisture content, volatile matter, ash content, and fixed carbon. The results of the proximate and ultimate analyses values are shown in Table 4.1. In view of the data of proximate analysis, raw peanut shell shows low moisture content (8.6%), high percentage of volatile matter (51.3%), average content of fixed carbon (33.2%) and low ash content (4.9%). Lori et al 2007 suggested that, High volatile matter content usually increases the carbon porosity in the carbonization stage while a low inorganic content is vital due to their abilities to produce a low ash and high fixed carbon content.

4.2.2 Ultimate analysis

The ultimate analysis of peanut shell involves the estimation of carbon, hydrogen, nitrogen, sulphur and oxygen. The results of ultimate analyses values which are shown in Table 4.1 showed that raw peanut shell has 39.5% of carbon, 9.21% hydrogen, 4.31% Nitrogen and 8.47% of oxygen.

The proximate analysis for peanut shell (Table 4.1) shows the presence of high amount of volatile mater and low ash content. The amount of inorganic components of carbon precursors has been reported to greatly influence porosity development of porous carbon by blocking pore entrances during the activation process (Yun et al 2002). And also at high temperatures, the volatile matters are completely removed. Thus the low ash content and high volatile matter suggested that Peanut shell has the potential to be activated carbon precursor.

Table 4.1 Proximate and ultimate analysis values of raw Peanut shell

Proximate Analysis (%)		**Ultimate Analysis** **(%)**	
moisture content	8.6	C	39.5
volatile matter	51.3	H	9.21
ash content	4.9	N	4.31
fixed carbon	33.2	O	8.47
		S	22.14

4.3 standard curve on methyl blue absorbance

Methyl blue is correlated with ability of activated carbon to adsorb colour and indicate developed mesoporosity of the AC. In order to use it as standard, appropriate concentration of this acid is taken and its absorbance is measured by spectrophotometer at 620nm and the curve generated from the plot of absorbance versus concentration.

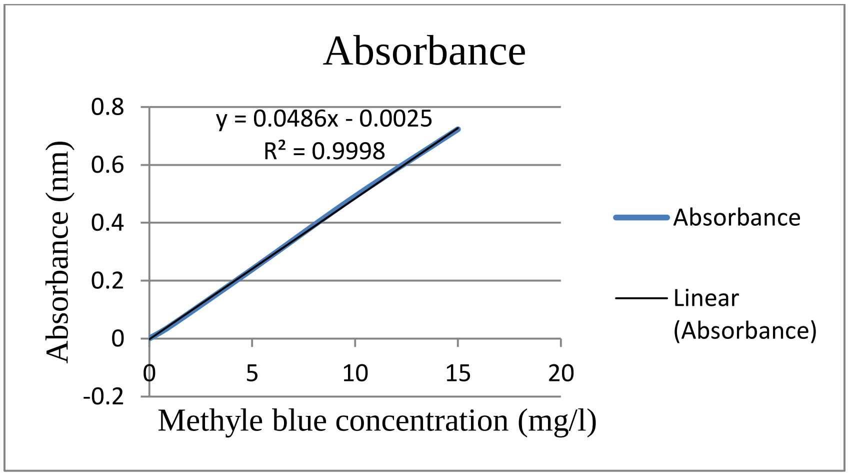


Fig 4.1: Standard Curve of Methyl Blue

From Fig 4.1 we deduced that absorbance versus concentration of the calibration curve is straight line having equation of the curve y = 0.0486x - 0.0025 with Regression coefficient of 0.9998.

This large number of R2 curve is successfully obtained. Based on this equation the adsorption efficiency was calculated and its absorbance value is given in the Appendix B.

4.4 Experimental Design and Statistical Data Analysis of Activated Carbon

Results for activated carbon production by using peanut shell as a precursor with different parameters such as temperature, particle size and impregnation chemical concentrations were evaluated on the effect of ash content and methylene blue number. There were about 17 numbers of experimental run as per by a standard Design-Expert 7.0.0 software Box-Behnken design (BBD) of response surface methodology (RSM).

Table 4. 2: Statistical analysis of activated carbon

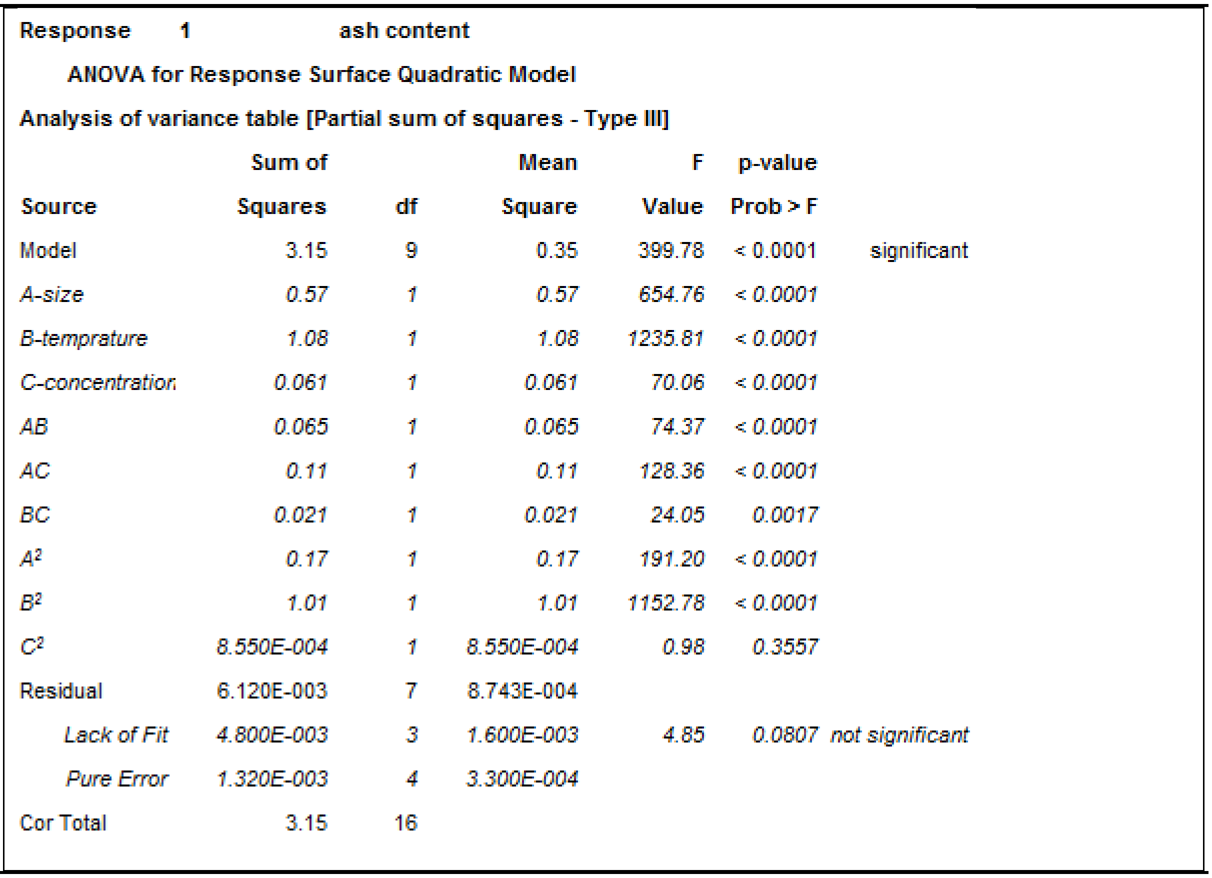
			Factor 1	Factor 2	Factor 3	Response 1	Response 2
Std	Run	Block	A:Particle Size	B:Activation Temperature	C:KOH Concentration	Ash Content	Methylene Blue Adsorption
			(mm)	^{o}C	Wt.%	%	%
1	3	Block 1	0.5	500	0.5	1.49	76.3
2	4	Block 1	2.5	500	0.5	2.47	61.3
3	10	Block 1	0.5	700	0.5	1.29	79.5
4	9	Block 1	2.5	700	0.5	1.56	74.5
5	5	Block 1	0.5	600	0.25	1.32	78.9
6	8	Block 1	2.5	600	0.25	2.15	65.2
7	2	Block 1	0.5	600	0.75	1.28	80.6
8	17	Block 1	2.5	600	0.75	1.54	74.9
9	13	Block 1	1.5	500	0.25	2.2	64.5
10	14	Block 1	1.5	700	0.25	1.73	72.3
11	1	Block 1	1.5	500	0.75	2.02	67.1
12	6	Block 1	1.5	700	0.75	1.35	81.2
13	11	Block 1	1.5	600	0.5	1.35	80.9
14	12	Block 1	1.5	600	0.5	1.32	81.0
15	7	Block 1	1.5	600	0.5	1.34	79.1
16	16	Block 1	1.5	600	0.5	1.37	81.2
17	15	Block 1	1.5	600	0.5	1.34	81.3

From the analysis of the above Table 4.2, it is observed that the maximum and minimum ash content is 2.47 and 1.28 respectively and 81.3% decolorization efficiency. Based on these results of the different parameters the relationship and the interaction of the combination of these parameters on the ash content and Methylene blue adsorption have been studied graphically.

4.4.1 Analysis of Variance for the Data (ANOVA)

The table below shows analysis of variance (ANOVA) obtained from design expert 7.0.0 software, which tells as the significance of different factors.

Table 4. 3: Design Expert Output (ANOVA) for Preparation of Activated Carbon



Response 1 ash content

ANOVA for Response Surface Quadratic 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	3.15	9	0.35	399.78	< 0.0001	significant
A-size	0.57	1	0.57	654.76	< 0.0001	
B-temprature	1.08	1	1.08	1235.81	< 0.0001	
C-concentratior	0.061	1	0.061	70.06	< 0.0001	
AB	0.065	1	0.065	74.37	< 0.0001	
AC	0.11	1	0.11	128.36	< 0.0001	
BC	0.021	1	0.021	24.05	0.0017	
A^2	0.17	1	0.17	191.20	< 0.0001	
B^2	1.01	1	1.01	1152.78	< 0.0001	
C^2	8.550E-004	1	8.550E-004	0.98	0.3557	
Residual	6.120E-003	7	8.743E-004			
Lack of Fit	4.800E-003	3	1.600E-003	4.85	0.0807	not significant
Pure Error	1.320E-003	4	3.300E-004			
Cor Total	3.15	16				

The Model F-value of 399.78 implies the model is significant. There is only a 0.01% 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, AB, AC, BC, A^2, B^2 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 work.

The "Lack of Fit F-value" of 4.85 implies there is a 8.07% chance that a "Lack of Fit F value" this large could occur due to noise. Lack of fit is bad -- we want the model to fit. This relatively low probabiity (<10%) is troubling.

Table 4.4 Predicted and Adjusted R-Squared

Std. Dev.	0.030	R-Squared	0.9981
Mean	1.67	Adj R-Squared	0.9956
C.V. %	1.77	Pred R-Squared	0.9750
PRESS	0.079	Adeq Precision	58.647

The "Pred R-Squared" of 0.9750 is in reasonable agreement with the "Adj R-Squared" of 0.9956. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 58.647 indicates an adequate signal. This model can be used to navigate the design space.

4.4.2 Regression Model Equation

Design-expert was applied to analyze results on the activated carbon and a first order regression equation, with the interaction terms, of the form, the final model equation in terms of coded factor was presented by equations representing the variation of ash content of AC with independent factors.

Final equation in terms of coded factors:

Ash content (%) $=+1.34+0.29*A -0.28* B-0.15 * C -0.18*A*B -0.14*A* C-0.050*B*C+0.053*A^2+0.31*B^2+0.18*C^2$ (4.1)

MB adsorption (%) $= +78.76-5.09 * A+4.53* B+2.76* C+2.50* A * B+1.68* A * C +1.05* B * C -0.69 * A^2 -5.17 * B^2 -2.84 * C^2$ (4.2)

Where A: Particle size, B: temprature and C: concentration

4.4.3 Diagnostic Test for the Response

Diagnosing of the statistical properties of the model after post ANOVA analysis is the necessary part before going for examining the model graphs and optimization. Normal probability plot of studentized residuals for the diagnosing for model adequacy checking, the data points should be approximately linear and a nonlinear pattern (look for an S-shaped curve) indicates non-normality in the error term. The normal probability plot, (Fig4.2), indicates the residuals following a normal distribution, in which case the points follow a straight line. This indicates the model satisfies the assumption of ANOVA.

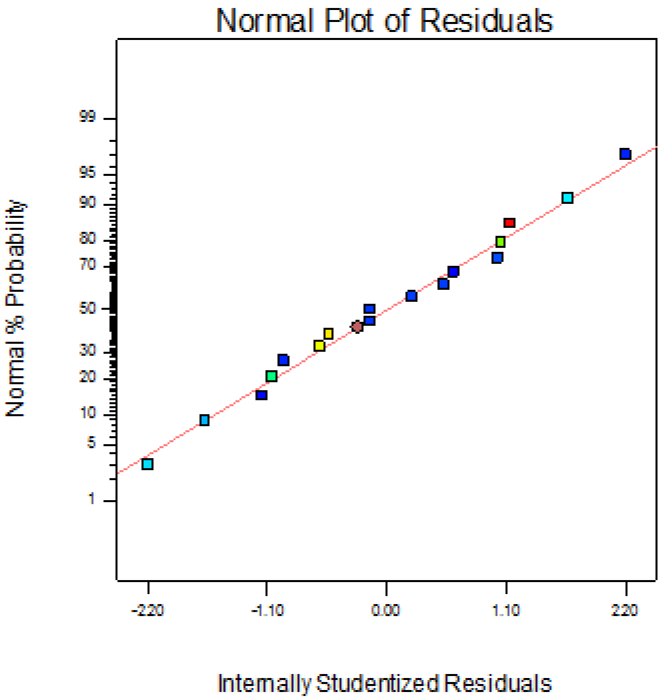
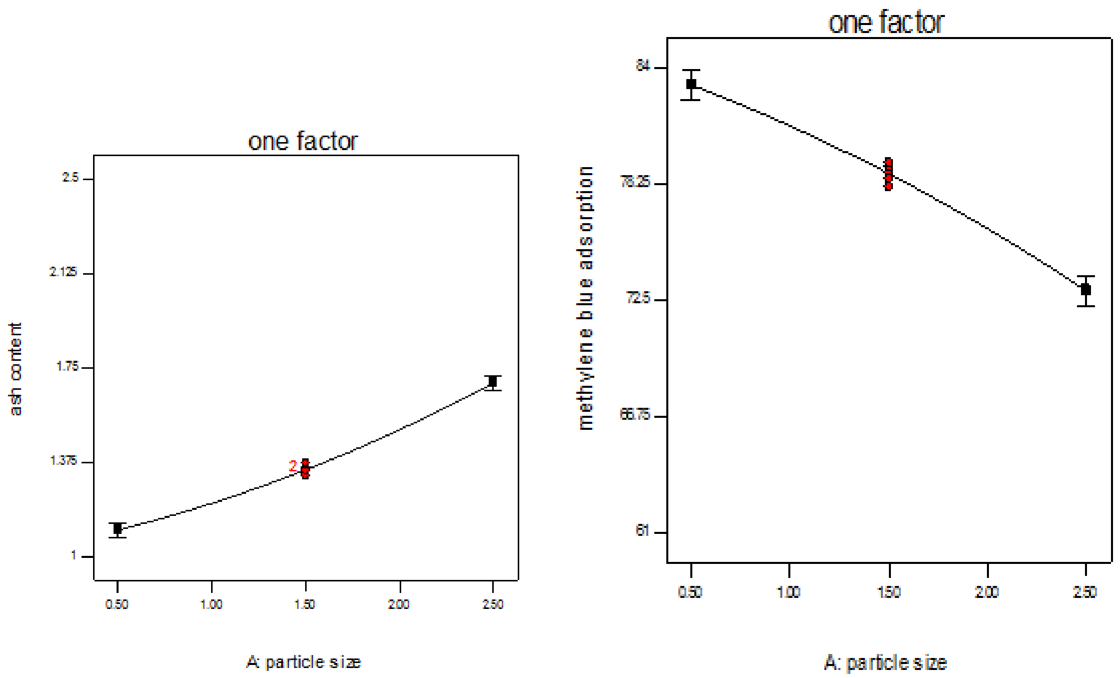


Fig 4.2: Diagnostic Test for the Response

4.5 Effect of process variables on Ash Content and Methyl Blue Adsorption (One Factor)

4.5.1 Effect of Particle Size on Ash Content and of Methyl Blue Adsorption

Fig 4.3(A) and Fig 4.3(B) shows the effect of particle size on ash content and Methylene blue adsorption efficiency of activated carbon respectively. It can be seen that as a particle size increase, the ash content also increased significantly and methylene blue adsorption efficiency also decreased. As a particle size decrease, the surface area of activated carbon increase. Due to this methylene blue adsorption increased with decreasing particle size. And also high amount of ash content for adsorbent is undesirable. Since it reduces the mechanical strength of activated carbon and affects methylene blue decolorization efficiency (Fig 4.3(B)).

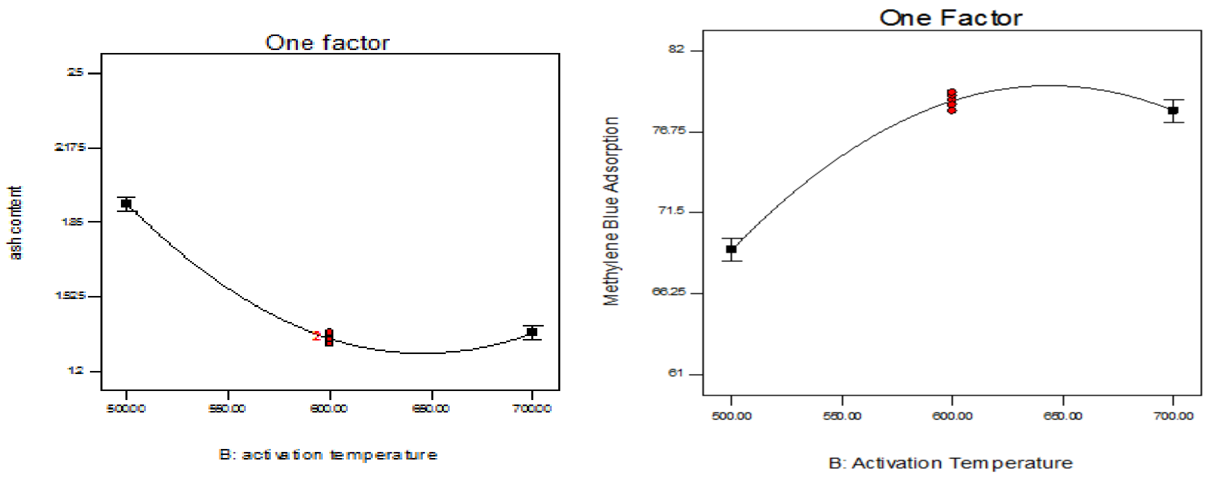


(A) (B)

Fig 4.3: Effect of particle size on (A) ash content and (B) methyl blue adsorption

4.5.2 Effect of Activation Temperature on Ash Content and MB Adsorption

The effect of temperature and the percent ash content of activated are shown in Fig 4.4(A) and (B) below. As shown in the figure the ash content of AC decrease gradually with rise in temperature in the range between 500°C to 600°C. when the activation temperature increased to 700°C ash content also increase. While increasing the activation temperature causes the enhancement of adsorption rate of activated carbon by increasing formation of porosity until it reaches at 600°C and then decreased when the temperature exceeds. This is due to conversion of carbon into gaseous products.

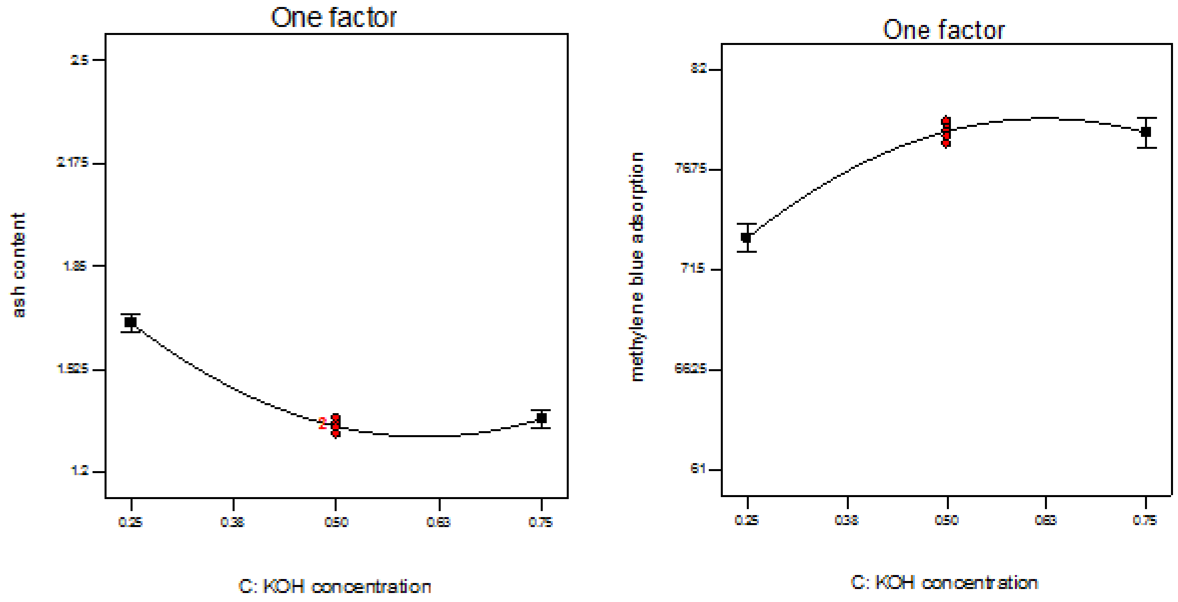


(A) (B)

Fig 4.4: Effect of Activation Temperature on (A) Ash content and (B) MB decolorization Efficiency

4.5.2 Effect of KOH Concentration on Ash Content & MB Adsorption

The influence of impregnation chemical concentration on the ash content and methyl blue adsorption of activated carbon is presented in Fig 4.4(A) & (B) respectively. As shown the Fig 4.5A, at lower KOH concentration, the percentage of ash content is high. It also shows that percentage of ash content decrease as the concentration of KOH increase in the range of 25 to 50 % w/w. while Fig 4.5(B) shows that methyl blue adsorption increased with increasing KOH concentration and reached at a maximum at 50% w/w. Further increasing in KOH concentration led to an increase on ash content and decrease for adsorption of methylene blue. This change is due to increasing concentration can cause mixing of raw material with activator agent to be difficult and at higher concentration, a larger swelling of the particle was produced but the distribution of KOH throughout the interior of the particle was poor.



(A) (B)

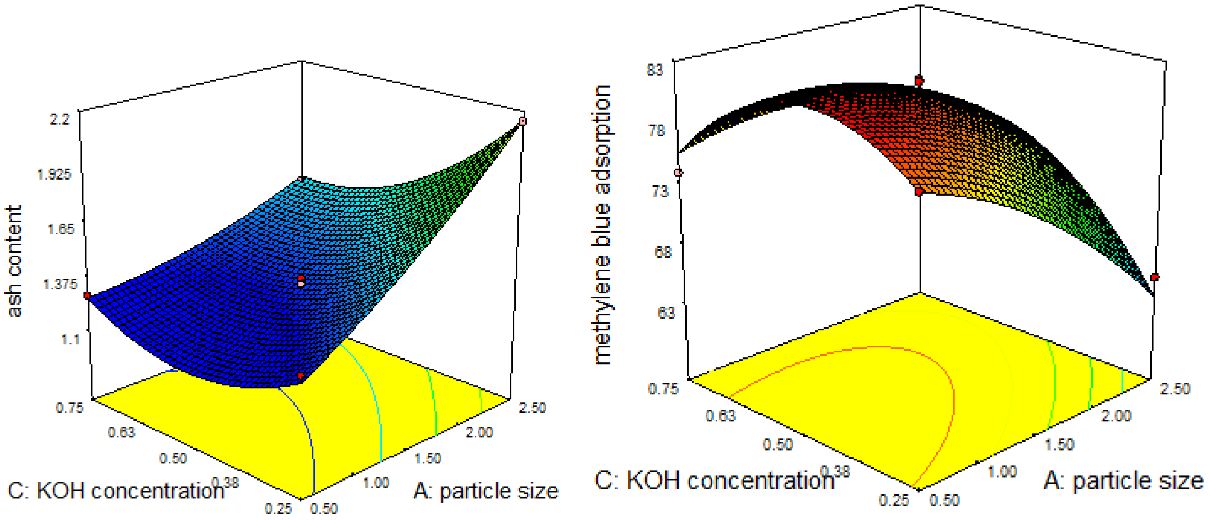
Fig 4.5 Effect of KOH concentration on (A) ash content & (B) methyl blue adsorption

4.4 Interaction Effects of Process parameters on the ash content and methylene blue

3D response surface plots which are the graphical results of interactive effects are shown in Fig 4.6 – 4.8. The process variables were found to have significant interaction effects. Fig 4.6, 4.7 and 4.8 shows the interaction between particle size to KOH concentration, activation temperature to KOH concentration and particle size to activation temperature respectively on the ash content and methylene blue adsorption efficiency of activated carbon.

Fig 4.6(A) & (B) represents the response for the interactive factors Particle size to KOH concentration on ash content and methylene blue adsorption efficiency of AC respectively. This Fig 4.6 (A) surface plot shows that the lowest ash content is obtained at the center of KOH concentration and lower particle size. However, above 50%w/w concentration led to an increase on ash content and decrease for methylene blue adsorption efficiency. This change is due to increasing concentration can cause to be difficult to distribution of KOH throughout the interior of the particle. While the decrease in the ash content of activated carbon at smaller particle size is due to having better mixing with the activation agent, the easier release of the inorganic and volatile materials are achieved during the activation process. The removal of volatiles attributed to lower inorganic content higher fixed carbon and to increase porosity.

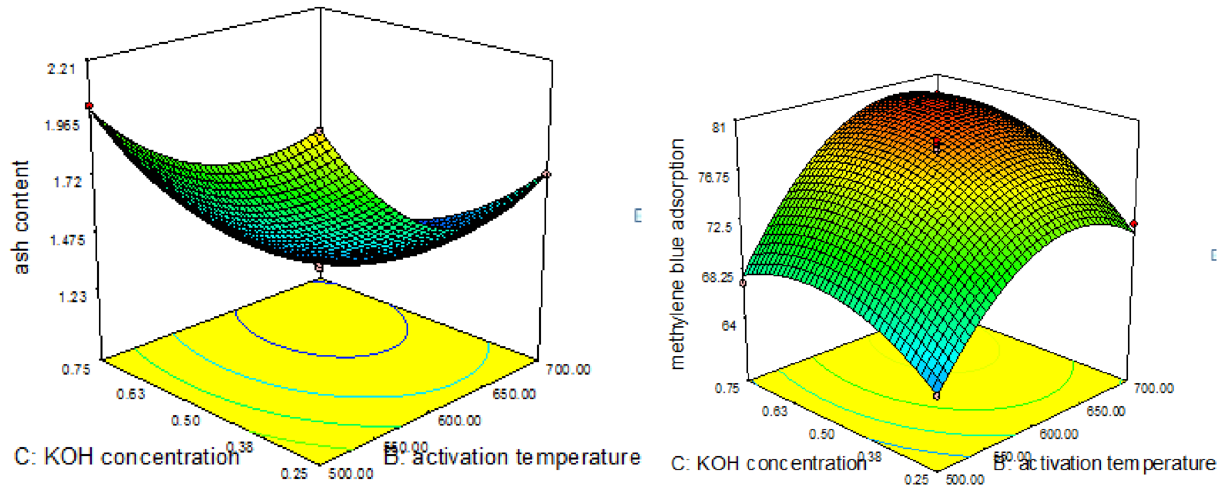
From Fig 4.6 (B) best efficiency of methylene blue adsorption was obtained at lower particle size and at the center of KOH concentration and also when we compare the ash content and methylene blue adsorption, they have direct relation.so the reason for this result is due to the same explanation for Fig 4.6 (A).



(A) (B)

Fig 4.6 Interaction effects of particle size to KOH concentration on (A) the ash content and (B) methylene blue adsorption

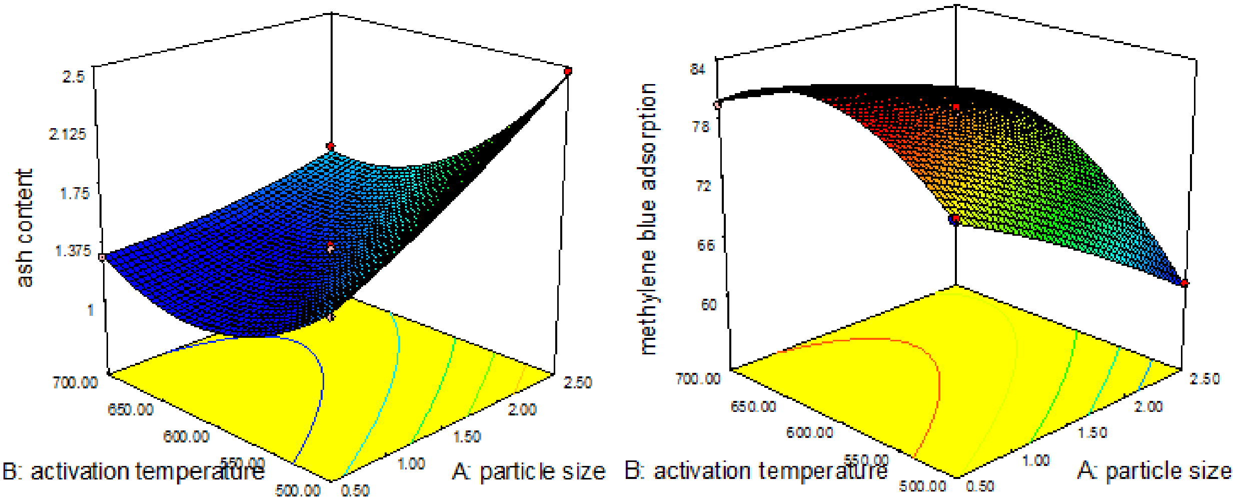
As the interaction graph of activation temperature and concentration indicated below in fig4.7 (A) for constant Particle size the ash content exhibits low at the center of KOH concentration and activation temperature and high methylene blue adsorption efficiency.as we explain in the above figure high KOH concentration is difficult to penetrate to the interior surface of raw material and low concentration is not enough to prepare the internal structure of raw material. While in Fig 4.7 (B) increasing temperature with increasing KOH concentration causes the enhancement of methylene blue adsorption efficiency. This behavior is due to more removal of volatile compounds by increasing temperature. However, at high temperature (above 600^{o}c) increasing temperature leads to demolish methylene blue adsorption efficiency because of demolish the porous structure of AC. Consequently methylene blue adsorption and ash content decreased with increasing KOH concentration and temperature.



(A) (B)

Fig 4.7 Interaction effects of KOH concentration to activation temperature on (A) the ash content and (B) methylene blue adsorption

Fig 4.8 (A) & (B) shows that the response for the interactive factors Particle size to activation temperature on ash content and methylene blue adsorption efficiency of AC respectively. As a particle size decrease, the temperature distribution becomes uniform to the interior of particle. Thus the surface area of activated carbon increased. However, at high temperature (above 600^{o}c) increasing temperature lead to demolish the porous structure of AC and losing weight of activated carbon and increase ash content. Consequently, methylene blue adsorption and ash content decreased with increasing particle size. And also temperature above 600oc gives undesirable ash content for adsorbent. Since it reduces the mechanical strength of activated carbon and affects methylene blue decolorization efficiency.



(A) (B)

Fig 4.8: Interaction effects of Activation Temperature and Particle size on (A) The Ash content and (B) MB Adsorption

4.6 Optimization of Process Variables

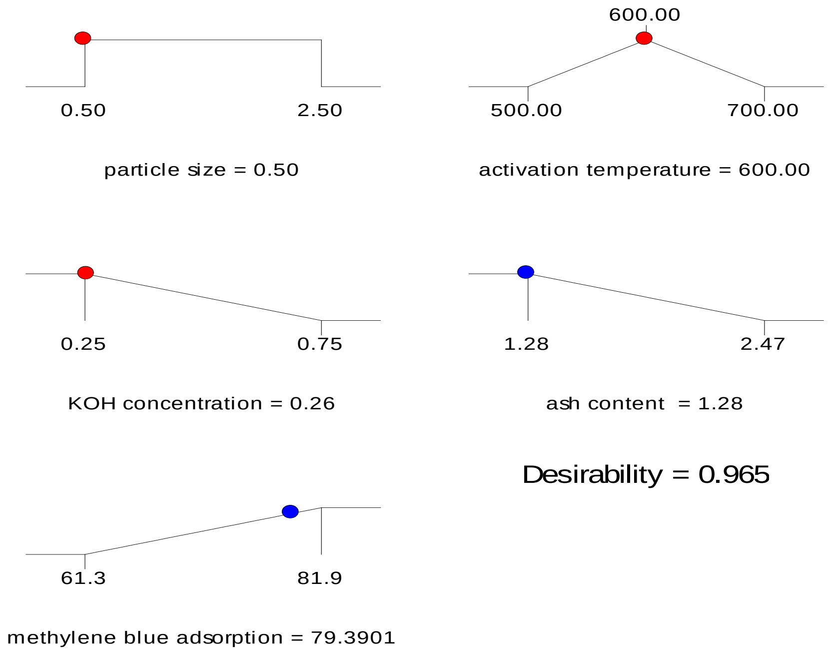
Within the scope this research, Optimization of process parameters which lead to an activated carbon with a good characteristic was carried out after observing all the effects of variables. It is to note that results obtained when studying the effect of individual parameters (activation temperature, particle size and KOH concentration) on the methylene blue adsorption and percentage of ash content. Table 4 .4 shows that, the optimum working conditions (ultimate goals, high and low limits) of the response and factors (activation temperature, particle size and KOH concentration) employed during the optimization analysis.

In view of the optimization, the targeted criterion was minimized for the percentage of ash content and increase methylene blue numbers while the factors values were set in the range studied.

Table 4. 5 Optimization constraints and solutions for activation parameter

Name	Goal	Lower Limit	Upper Limit
particle size	is in range	0.5	2.5
activation temperature (^oC)	is target=600	500	700
KOH concentration	minimize	0.25	0.75
ash content	minimize	1.28	2.47
methylene blue adsorption	maximize	61.3	81.9

No	**particle size**	**activation temperature**	**KOH Concentration**	**Ash content**	**MB Adsorption**	**Desirability**	
1	0.50	600.00	0.26	1.28001	79.3901	0.965	Selected
2	0.50	600.00	0.25	1.2861	79.2749	0.964	
3	0.50	600.00	0.30	1.22691	80.5056	0.957	



Based on the optimization result peanut shell at 0.5mm particle size, 0.30%.wt KOH concentration and activate at 600°C can give the best granular activated carbon with high colour removal efficiency (79.3901) and low ash content (1.28).

4.7 Characterization results of activated carbon

After selecting the activated carbon with low ash content and methyl blue adsorption, the selected granular activated carbon characterization which are FTIR, ultimate analysis, proximate analysis and PH value were done and the results discussed as follow.

4.7.1 Proximate and Ultimate analysis

The results of ultimate and proximate analyses of the granular activated carbon (GAC) are shown in Table 4.4. When we compare the raw material and GAC, Table 4.1, it can be seen that a starting material for granular activated carbons, the peanut shell has (4.9%) ash content, 51.3% volatile mater, 8.6% moisture content and (33.2%) carbon content. After activation (Table 4.3) shows, ash content had decreased to 1.28% while the volatile mater decreased to 3.2%. Less percentage of volatile matter represents the completion of the carbonization process leaving more fixed carbon in the carbonaceous sample 81.5%.and it reflects on the total carbon present in the product.

The comparison of raw material with AC of ultimate analysis in terms of the non-carbon elements (hydrogen, oxygen, traces of nitrogen and sulfur), the result (Table 4.4) shows that almost all non- carbon elements are removed while the total amount of carbon present in the raw material was improved after activation process. It has 81.5% fixed carbon. Decomposition occurred since the volatile compounds could not maintain its stability at high temperatures, the volatile matter such as hydrogen (H), nitrogen (N) and oxygen (O) are almost removed during carbonization leaving only the portion of stable carbon as residues. This indicates marginal variation especially in the volatile matter and fixed carbon. Therefor based on the result of proximate and ultimate analysis the selected activated carbon can be a good adsorbent with high carbon content and low ash content.

Table 4.5 Proximate and ultimate analysis values of activated carbon

Proximate Analysis (%)		Ultimate Analysis (%)	
moisture content	3.5	C	83.4
volatile matter	3.2	H	1.62
ash content	1.28	N	1.11
fixed carbon	81.5	O	2.34
		S	-

4.7.2 Fourier Transforms Infrared Spectroscopy Analysis (FTIR)

The characteristic functional groups of the AC and raw material (peanut shell) were investigated using FTIR spectra as identification tool. The surface chemistry of an AC was determined by the type, quality and bonding of functional group. The increase and decreases in the spectrum peaks shows how the experimental conditions affect the structure of material. Mastalerz and Bustin, 1995 states that the spectra of carbon samples could be analyzed in terms of the fixed mix of functional groups. OH and NH stretching in between 3100 - 3500 cm-1, C-H aromatic in between 3000 - 3100 cm-1, C-H aliphatic in between 2800 - 3000 cm-1, C=O and C-O stretching in between 1640 - 1750 cm-1 attributed to phenolic ester, carboxylic acid and conjugated ketonic structures. The region in between 700 - 900 cm-1 contains various bands related to aromatic, out of plane C-H bending with different degrees of substitution.

Fig 4.8 shows the spectra of the raw peanut shell, and Fig 4.9 shows the spectra of granular activated carbon. These FTIR spectra reflect the differences between raw peanut shell and AC. Significant changes in the spectra of Raw material and activated products are observed which, in particular, spectrum of the starting material shows many peaks belonging different functional groups. The wide peak, which appears between 1000 and 1150 cm−1, is related with ash composition and side peaks at 1109 and 1160–1260 cm−1 belong to alcoholic and phenolic groups.

According to Yacob et al., the functional groups from the raw material were released as volatile materials when heat was supplied to the sample during the carbonization and activation process. This proved that the activation process has taken place successfully. However, the chemical activated carbon retained some IR sensitive functional groups, C-O functional group.

Therefore, the prepared materials are mainly composed of amorphous carbons with different oxygen containing surface groups. These carbon–oxygen groups may exercise a profound effect on the surface properties of ACs and thus influence their adsorption characteristics, that is, these groups could be the potential active sites for the interaction with the adsorbate.

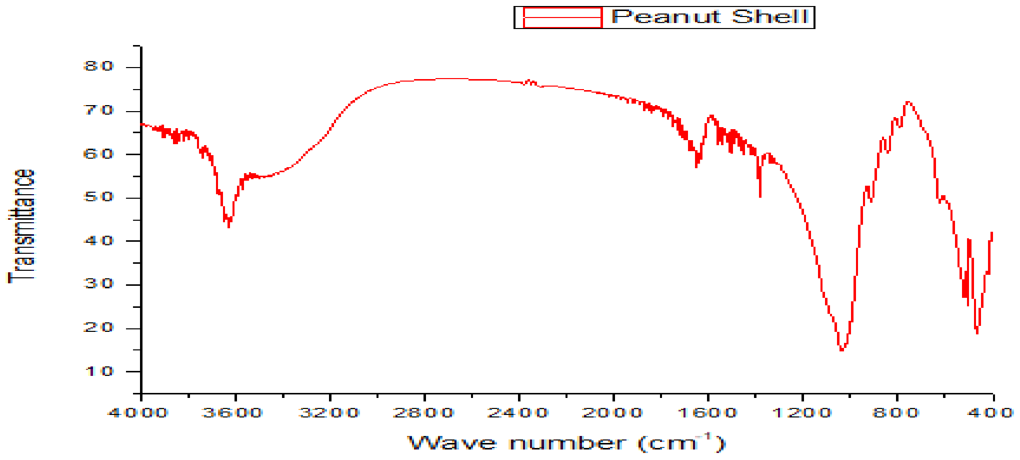


Fig 4.8 FTIR spectra of peanut shell

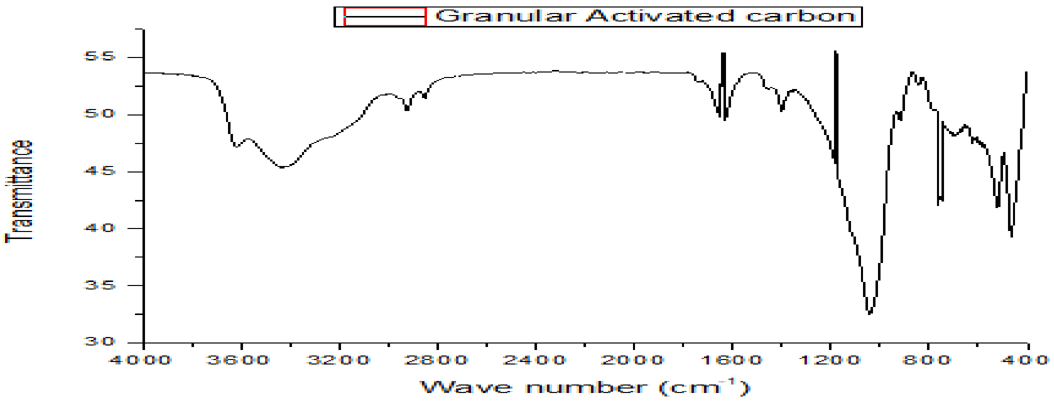


Fig 4.9: FTIR Spectra of Granular Activated Carbon

4.7.3 Point of zero charge (pzc)

pHpzc is the pH of the aqueous solution in which the solid presents a neutral electric potential, pH at which the initial value is the same as the final value. pHinitial < pHfinal shows the effect is positive charge, pHinitial > pHfinal shows negative charge, for both cases the result indicated that the activated carbon surface is positively charged and negative charge respectively. The values have been acceptable since the positive charge and negative charge means the liquid has no pipe scaling and corrosion effect. The pzc was obtained by acid-base titrations by monitoring the pH at the values of 5.5, 6.0, 7.0, 7.5, 8.0 & 8.5 and shaking it for 24hrs. The results are plotted with pH final – pH initial against pH final. The point at which pH = 0 is known as pH ZPC.

Table 4.6 Point of zero charge

No.	$pH_{initial}$	pH_{final}	Result
1	5.5	5.0	Negative charge
2	6.0	5.4	Negative charge
3	6.5	6.9	Positive charge
4	7.0	8.1	Positive charge
5	7.5	7.9	Positive charge
6	8.0	8	pzc
7	8.5	9.0	Positive charge

4.7.4 The activated carbon pH measurement

The pH value of activated carbon was measured by using pH meter after agitated for 24hrs.the obtained pH value is 7.1. Bernardin (1985) reported that, in sugar decolorization, a distinctly acidic activated carbon may cause inversion of sucrose, and a distinctly alkaline carbon may cause color development through alkaline degradation of organic impurities. Depending on sugar inversion and zero point of charge these pH value is accepted for adsorption process.

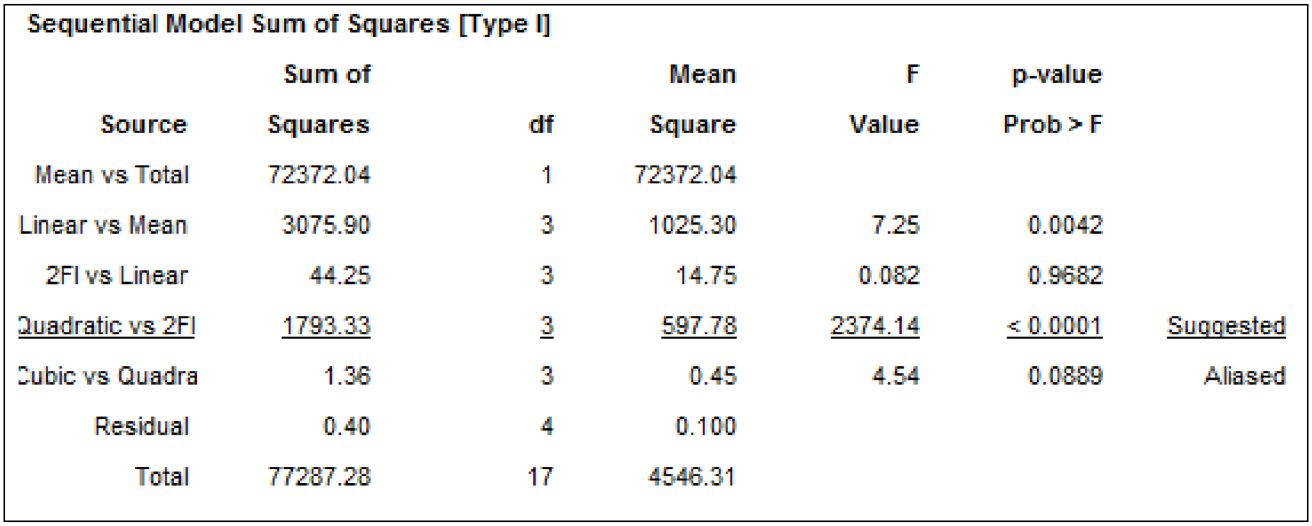
4.8 Adsorption of Cane Syrup colorants on Activated carbon

4.8.1 Statistical Analysis on decolorization efficiency

Optimization of the decolorization parameters was done using the chosen Granular activated carbon. Optimization was carried out using BBD design with three factors (carbon dosage, time and syrup temperature) and one response (decolorization efficiency). Statistical analysis was carried out to determine correlation coefficients of the model as a function of the responses. The statistical summary of the design and the Experimental Design are shown in Appendix B.

Table 4.7 shows sequential model sum of squares for percentage of decolorization efficiency of cane sugar syrup. The models were chosen because of their high correlation coefficient (actual and adjusted) value as shown in Appendix B.

Table 4. 7: Sequential Model Sum of Squares for cane syrup decolorization efficiency



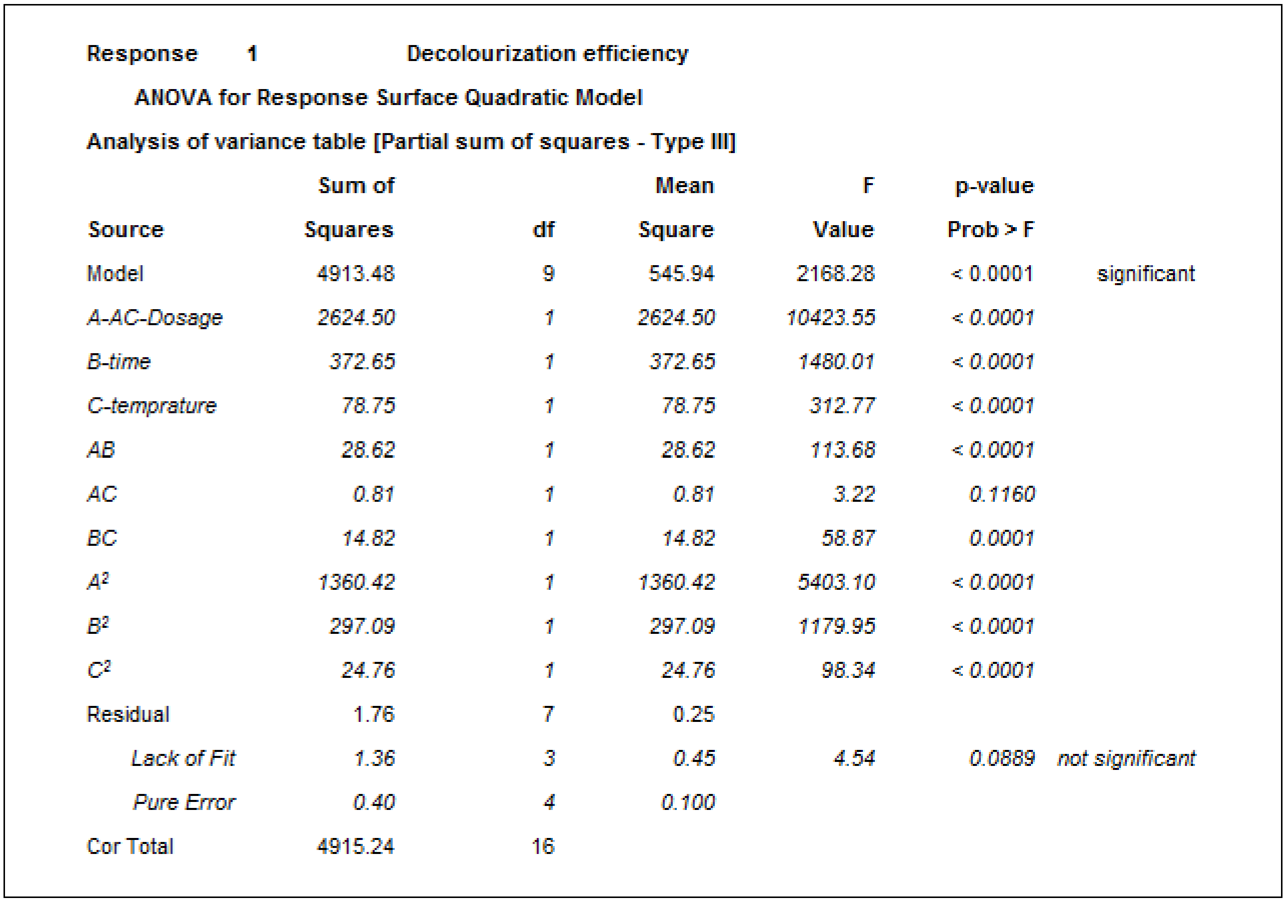
Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	72372.04	1	72372.04			
Linear vs Mean	3075.90	3	1025.30	7.25	0.0042	
2FI vs Linear	44.25	3	14.75	0.082	0.9682	
Quadratic vs 2FI	1793.33	3	597.78	2374.14	< 0.0001	Suggested
Cubic vs Quadra	1.36	3	0.45	4.54	0.0889	Aliased
Residual	0.40	4	0.100			
Total	77287.28	17	4546.31			

4.8.3 Test for Significance and Accuracy of the Model

The levels of significance of the models were tested using the p-value. The Model F-value of 2168.28 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Table 4. 8: Analyses of Variance for response surface 2FI model for Decolorization efficiency of cane syrup



Response 1 Decolourization efficiency

ANOVA for Response Surface Quadratic 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	4913.48	9	545.94	2168.28	< 0.0001	significant
A-AC-Dosage	*2624.50*	*1*	*2624.50*	*10423.55*	*< 0.0001*	
B-time	*372.65*	*1*	*372.65*	*1480.01*	*< 0.0001*	
C-temprature	*78.75*	*1*	*78.75*	*312.77*	*< 0.0001*	
AB	*28.62*	*1*	*28.62*	*113.68*	*< 0.0001*	
AC	*0.81*	*1*	*0.81*	*3.22*	*0.1160*	
BC	*14.82*	*1*	*14.82*	*58.87*	*0.0001*	
A^2	*1360.42*	*1*	*1360.42*	*5403.10*	*< 0.0001*	
B^2	*297.09*	*1*	*297.09*	*1179.95*	*< 0.0001*	
C^2	*24.76*	*1*	*24.76*	*98.34*	*< 0.0001*	
Residual	1.76	7	0.25			
Lack of Fit	*1.36*	*3*	*0.45*	*4.54*	*0.0889*	*not significant*
Pure Error	*0.40*	*4*	*0.100*			
Cor Total	4915.24	16				

As shown in Table 4.78, P-value less than 0.05 indicate the model terms are significant and p-values greater than 0.1 indicate model terms are not significant. it can be seen that the model terms A, B, C, AB, and BC are significant. Values of "Prob > F" less than 0.0500 indicate model terms are significant.

The "Lack of Fit F-value" of 4.54 implies there is a 8.89% chance that a "Lack of Fit F-value" this large could occur due to noise. Lack of fit is bad. we want the model to fit This relatively low probabiity (<10%) is troubling.

Normal probability plots of the residuals are shown in Appendix B. Since the residuals lie approximately along a straight line, any problem was not suspect with normality in the data. There are no indications of severe outliers.

4.8.4 Development of regression model equation

The equations generated from the fitted surface response 2FI and quadratic models for the decolorization efficiency of cane syrup is shown in Equations (4.3). Kumar et al. (2008) stated that when regression coefficient has a positive sign, the increase of the associated factor causes an increase in response and a negative sign would cause a decrease in the optimization parameter.

Final Equation in Terms of Actual Factors:

Decolourization efficiency =-88.26250+86.01250* AC-Dosage+1.17200 * time+0.98250*temprature+0.10700 * AC-Dosage * time-0.030000 * AC Dosage * temprature+5.13333E-003 * time * temprature -17.97500 * AC-Dosage^2-0.013440* time^2-0.010778 * temprature^2 (4.3)

4.8.5 Effect of Individual Parameters on Decolorization Efficiency

Fig 4.10- 4.12 show the effect of individual parameters on decolorization efficiency of cane syrup. It is observed that the bleaching power of the adsorbent and effect of each factor varies from one parameter to others.

As shown in the Fig 4.10, the decolorization efficiency of activated carbon is positively affected by temperature. As temperature increase the percentage of decolorization efficiency increase. The increase of temperature can increase the mobility of colorants and the surface becomes activated and adsorption capacity increases (Hameed et el.(2007). However, the results clearly indicate that the decolorization efficiency increases to an optimum value from which further increase in the temperature has no significant effect on them.

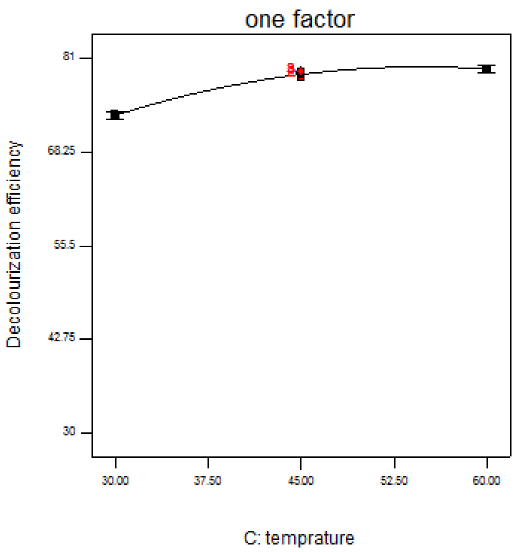


Fig 4.10: Effect of temperature on decolorization efficiency

As shown in Fig 11, rate of adsorption of color was initially rapid, and progresses much more stable and reaches equilibrium. Once equilibrium was reached, there was no significant increase in the decolorization efficiency. The percentage color reduction reaches equilibrium almost after 50 min. The rapid increase of initial decolorization efficiency is due to at the beginning color is adsorbed by the exterior surface of AC. when the exterior adsorption surface reached saturation, the colorant enters in to the pores of adsorbent and is adsorbed by the interior surface of particle.

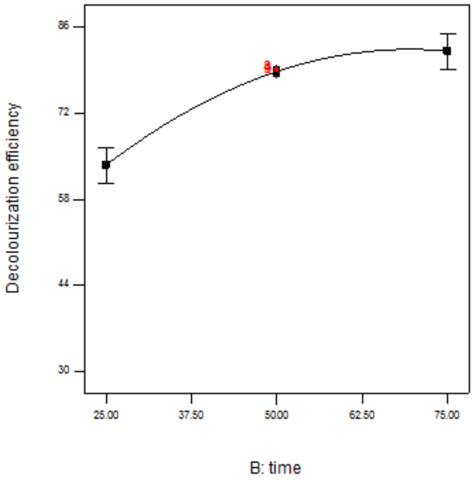


Fig 4.11: Effect of Time on Decolorization Efficiency

It is also observed that the bleaching power increases with the increase in activated carbon dosage. From Fig 12, it can be shown that the decolorization efficiency is mainly affected by carbon dosage. It was observed that increasing the activated carbon dosage increased the bleaching efficiency. Further increasing adsorbent led to an insignificant change in color reduction.

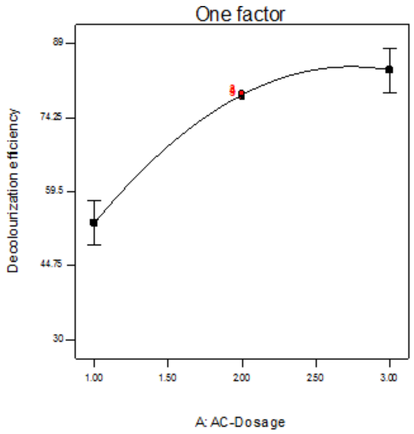


Fig 4.12: Effect of AC dosage on Decolorization Efficiency

4.8.6 Effect of Interaction between Process Variables

3D response surface plots which are the graphical results of interactive effects are shown in Figures 4.13 – 4.15. This representation showed that the relative effect of any two variables when the remaining variable kept constant. Fig 4.13 shows the effect of bleaching temperature and time interaction effect on decolorization efficiency. Both bleaching temperature and time have positive effect for color reduction on cane syrup. However, high bleaching efficiency occurs at the center point of bleaching temperature and time. It is seen from the figures that above 600^0C and 50min there is no significant change on color reduction. Percentage color reduction becomes constant. This is due to similar explanation given in the one factor effect.

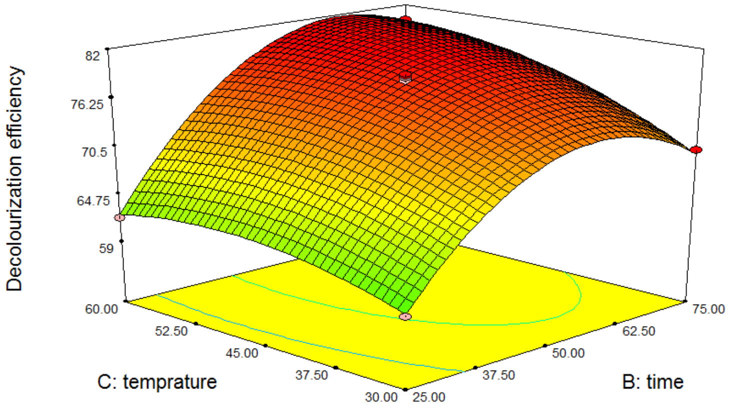


Fig 4.13: Response Surface Plots of Time and Bleaching Temperature For Color Removal

Fig 4.14 shows the responses for the interaction of temperature and AC dosage on cane sugar. The 3D response plot Fig 4.14 indicates that the percentage bleached increased when dosage increased. Increase in temperature showed insignificant change in the percentage bleached. Both factors have significant individual but not interaction effect on bleaching performance for cane syrup decolorization.

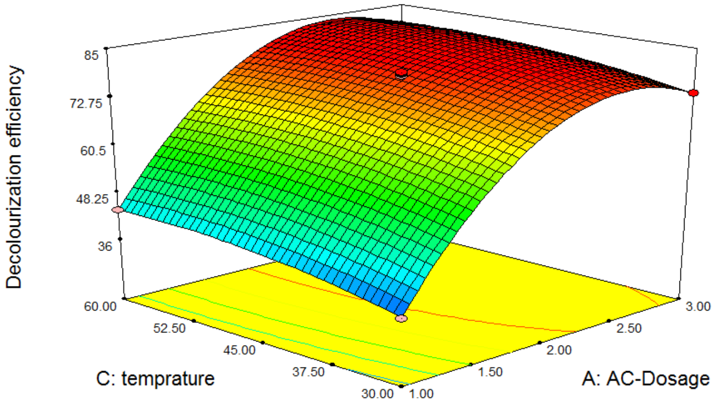


Fig 4.14: response surface plots of temperature and AC dosage for color removal

Fig 4.15 shows the percentage color reduction as a function of time and AC-dosage under experimental conditions. It can be seen that higher percentage bleached occurred at a higher dosage. Thus, dosage is the most important factor in improving the removal of undesired colors in cane syrup. Increase in percentage bleached as a result of increase in dosage is because of the more surface area available, which will accommodate more undesired colorants. This is due to similar explanation given in the one factor effect. After it reaches at equilibrium further increasing both AC-dosage and time can led to an insignificant change in color reduction.

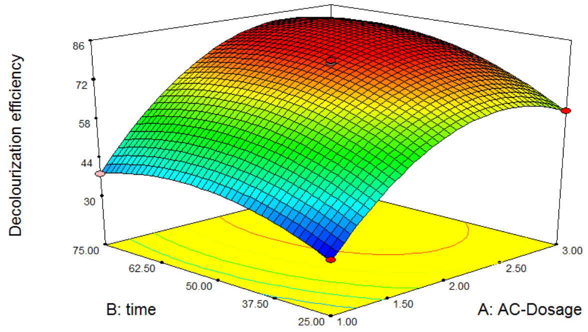


Fig 4.15: Response Surface Plots of Time and AC Dosage for Color Removal

4.8.7 Finding the optimal bleaching process parameters for cane syrup

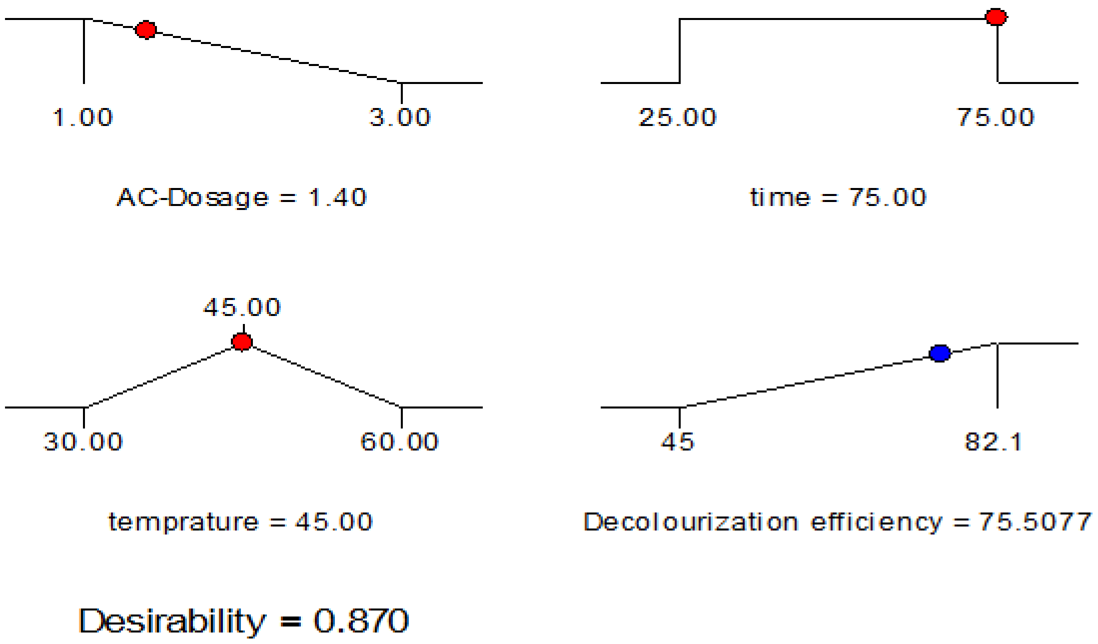
Optimization was carried out after observing all the effects of color removal. The objective is to maximize decolorization efficiency. Thirty solutions were found and the solution with the highest desirability was chosen. In other to verify the optimization results, the selected parameters were validated in the laboratory with suggested values as shown in Table 4.16. The result from the experiments confirmed the selected solutions.

Table 4. 9 Optimization constraints for decolorization efficiency

Name	Goal	Lower Limit	Upper Limit
AC-Dosage	minimize	1	3
time	is in range	25	75
temprature	is target=45^{o}c	30	60
Decolourization efficiency	maximize	45	82.1

Solutions

Number	**AC-Dosag**	**time**	**Tempratur**	**Decolourization Efficiency**	**Desirability**	
1	**1.40**	**75.00**	**45.00**	**75.5077**	**0.870**	**Selected**
2	**1.39**	**74.98**	**45.00**	**75.3471**	**0.869**	



The desired set of syrup decolorization parameters was determined through optimization of the responses. Accordingly, bleaching temperature of 45°C, bleaching time of 45min and 1.4 g granular activated carbon dosage were selected with 0.870 of desirability to predict decolorization efficiency.

Chapter Five

Conclusion and Recommendation

5.1 Conclusion

The highest adsorption capacity and low percent of ash content of activated carbon were investigated by means of BBD surface response. The use of peanut shell as a precursor for the preparation of activated carbons using KOH as an impregnation chemical was analyzed in detail. The influences of several variables such as: activation temperature, particle size and KOH concentration for 2hr activation time. The experimental data showed that the maximum adsorption of methylene blue and minimum ash content of were obtained and the optimization result shows that at 0.26%wt.KOH concentration, 0.5mm particle size and 600^{o}C activation temperature can get 79.4 methylene blue adsorption and 1.28% ash content.

The effects of activation on peanut shell structural properties were determined by elemental analysis, ultimate analysis, methylene blue adsorption and Fourier transform infrared (FT-IR). FTIR analysis identified the presence of carbonyls, alkenes and hydroxyls. These carbon–oxygen groups may exercise a profound effect on the surface properties of GACs and thus influence their adsorption characteristics. These groups have the potential active sites for the interaction with the adsorbate.

The proximate and ultimate analysis of activated carbon showed high percentage of carbon (81.5%), low volatile matters such as: 1.63% hydrogen, 1.11% nitrogen and 2.34% oxygen likewise low percentage of ash content (1.28%) which indicates that less percentage of volatile matters represents the completion of the carbonization process. Therefore based on the result of proximate and ultimate analysis the selected activated carbon can be a good adsorbent with high carbon content and low ash content.

The bleaching performance of the activated carbon on cane syrup decolorization was determined with respect to bleaching temperature, contact time and activated carbon dosage (AC). The results show that Optimum conditions are 45°C, 75min and 1.4%wt. AC dosage for 75.5% decolorization efficiency with 0.870of desirability. The overall results lead to conclude that peanut shell can be converted into good adsorbents by optimum chemical activation for bleaching of cane syrup, and thus represent a value-added to importing sugar quality and waste minimization.

5.2 Recommendation

If some further research work is carried out to explore the potential of peanut shell, recommended studies are listed below:

- ✓ It is recommended to regenerate granular activated carbon with the safest method for both the labor, equipment and with low cost used in sugar industry.
- ✓ Determination of the bleaching capacity using adsorption isotherm models and kinetic adsorption in order to examine the controlling mechanism of the adsorption process also suggested.
- ✓ It is recommended to perform preliminary design, economic feasibility study and establish economic scale for activated carbon manufacturing unit.

Reference

A. Bota, K.Laszlo, L .Nagy, G.Lajos, T. Copitzky, J. Langmuir ,**1997**, 13, 6502.

Agudo, J.A.G., Cubero, M.T.G., Benito, G.G., Miranda, M.P., (2002). Removal of coloured compounds from sugar solutions by adsorption onto anionic resins: equilibrium and kinetic study. Sep. Purif. Technol. 29, 199–205.

Ahari D., J. Genetole, 1961, La coloration en sucrerie: perfectionnements apportes a sa mesure, Ind. Alimentaires. et Agricoles., 742-747

Anonymous.1996. Sulfur Dioxide, Food Chemicals Codex, 4th edition. NationalAcademyPress

Arulkumar M, Sathishkumar P, Palvannan T (2011) Journal of Hazardous Materials 186: 827-834.

Ahmedna M, S.J Clarke, RM Rao, WE Marshall, M.M Johns, “ Use of filtration and buffers in raw sugar color measurement , J, Sci Food, Agric, 75, 109-116

Ahmadpour, A. and Do, D.D. 1996. The preparation of activated carbon from coal by chemical and physical activation, Carbon 34: 471-479.

Ahmadpour, A., Do, D. The preparation of activated carbon from macadamia nutshell by chemical activation. Carbon, 35, 1997, 1723-1732.

Albrecht, W. J. 1979 Peanut Hulls: Their Properties and Potential Uses. Agricultural Reviews and Manuals, ARM-S-1, 1(5)

Aworn, A., Thiravetyan, P., Nakbanpote, W. Preparation of CO2 activated carbon from corncob for methylene glycol adsorption. Colloids and Surfaces A: Physicochemical Engineering Aspects, 333, 2009, 19-25.

Babel, S., Kurniawan, T.A. Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. Chemosphere, 54 (7), 2004, 951-967.

Bansal, R.C., Donnet, J.B., Stoeckli, H.F. Active carbon. Marcel Dekker, 1988, New York.

Bonilla S.H., Almeida C.M.V.B., Giannetti B.F. and Huisingh D. (2010), The roles of cleaner production in the sustainable development of modern societies: an introduction to this special issue. Journal of Cleaner Production 1: 1-5.

Bernardin, Jr., F.E. (1985). Experimental design and testing of adsorption and adsorbates. Ch. 1 In Adsorption Technology: A Step-bystep Approach to Process Evaluation and Application. Chemical Industries 19. F.L. Sleijko (ed). p. 37-90. Marcel Dekker, Inc. N.Y.

Cookson, J.T. (1978). Adsorption mechanisms: the chemistry of organic adsorption on active carbon. Ch. 7. In Carbon Adsorption Handbook, P.N. Cheremisinoff and F. Ellerbusch (eds.), p. 241-279. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

B. Pendyal,(1998). Removal of sugar colorants by granular activated carbons made from binders and agricultural by-products.

Cerminara, P.J., Sorial, G.A., Papadimas, S.P., Suidan, M.T., Moteleb, M.A., Speth, T.F. Effect of influent oxygen concentration on the GAC adsorption of VOCs in the presence of BOM. Water Research, 29 (2), 1995, 409-419.

Coca, M., Teresa García, M., González, G., Peña, M., & García, J. A. (2004). Study of coloured components formed in sugar beet processing. Food Chemistry, 86, 421-433.

Cook, D., Newcombe, G., Sztajnbok, P. The application of powdered activated carbon for mib and geosmin removal: predicting pac doses in four raw waters. Water Research, 35 (5), 2001, 1325-1333.

Clarke, M. A., R. S. Blanco, and M.A. Godshall. (1984). Color test and other indicators of raw sugar refining characteristics. Proc. 1984 Sugar Processing Research Conference. New Orleans, LA.

C.P Huang, P.N. Cheremis, F. Ellerbusch, Carbon Adsorption Handbook, second ed., J Ann. Arbor Sci. Pub., Inc., Michigan, **1980**

F. Rodriguez-Reinoso , 1997 Introduction to carbon Technologies. Marsh, H., Heintz, E.A., Rodriguez- Reinoso, F. Eds., Publicaciones Universidad de Alicante.

G. U. Raju, S. Kumarappa, and V. N. Gaitonde, 2012 “Mechanical and physical characterization of agricultural waste reinforced polymer composites,” Journal of Materials and Environmental Science, vol. 3, no. 5, pp. 907–916,.

Hammed B H., Ahmad A A. Aziz N., 2007 isotherms, kinatics and thermodynamics of acid dye adsorption on activated palm ash.

Hassler, J. W, 1974.. Purification with activated carbon, 3rd ed., Chemical Publishing Co, Inc., NewYork.

Kostecki, John A., (1964). "The Kinetics of Physical Adsorption of Liquid Water from Benzene in Fixed-Bed Adsorbent Columns," Ph.D. Dissertation, Carnegie Institute of Technology

Lindeman, P. F., & O'Shea, M. G. (2004). Colorant removal during clarification and decolourisation processes. Proceedings of the Australian Society of Sugar Cane Technologists, 26, 51-64.

L. S. Singer, 1961, p. 37-64, in Proceedings of the fifth conference on carbon, Volume 2, Symposium Publications Division, Pergamon Press, 1963.

L. Wang, W. R. Zhao, and Z. B. Wu, , 2007 “Simultaneous absorption of NO and SO2 by Fe (II) EDTA combined with Na2SO3 solution,”Chemical Engineering Journal, vol. 132, pp. 227–232, 2007.

Macías-garcía A, Cuerda-correa EM, Olivares-marín M, Díaz-paralejo A, Díaz-díez MÁ: A preliminary study.J. Industrial Crops and Products.2012;35:105-110.

Mantell, C. L. (1946). Industrial Carbon: Its Elemental, Adsorptive and Manufactured Forms, Second edition. D Van Nostrand Company Inc. ew York.

Mastalerz M, Bustin RM (1995). Application of Reflectance Micro- Transform Infrared Spectrometry in Studying Coal Macerals Fuel, 74: 536-542.

Marsh, H., (2006),“Activated carbon’’, 1st Ed., Francisco Rodriguez-Reinoso, pp. 16, 182-183.

Mersad A.,Lewandowski R.,Hend, B. and declous M., (2003). Colorants in sugar industry:laboratory preparation and spectrometric analysis. Int. sugar. J., 105(1254),269-281.

Mohamed Ahmedna,(2000). Granular activated carbons from agricultural byproducts: preparation, properties, and application in cane sugar refining.

O. P. Fapetu, 2000 Production of carbon from biomass for industrial and metallurgical processes. Nigerian Journal of Eng. Manag.1, , 34- 37.

Parker K. J., J.C. William, 1968, Proc. of Tec. Sess. Cane Sug. Ref. Res., 117-128

Paton N.H., R. J. Mc Cowage, 1987, Colour forming mechanisms during mill processing, Proc. Aust. S.S.C.T. Conf., 11-20

Paton N.H., P. Smith, 1983, An HPLC study of the changes in colorant composition

Prahas, D., Kartika, Y., Indraswati, N., Ismadji, S. Activated carbon from jackfruit peel waste by

H3PO4 chemical activation: Pore structure and surface chemistry characterization. Chemical Engineering Journal, 140, 2008, 32-42.

Punsuwan, N. 2002. Preparation and characterization of activated carbon from lignite coal and bagasse by chemical.

R. C. Bamsal, J.B. Donnet, and F. Stocheti, 1998 “Active Carbon” MezzelDekker, New York, , pp. 245.

Riffer, R. (Ed.). (1988). The Nature of Colorants in Sugarcane and Cane Sugar Manufacture. Amsterdam: Elsevier.

S. Gueu, ‘‘Traitement 2007 de la pollution métallique et organique par les charbons actifs des coques de noix decoco et des graines de palmistes,’’ Thèse de Doctorat, Université de Cocody-Abidjan, pp. 5-20,

SB DAVIS Sugar Milling Research Institute, University of Natal, Durban, 4041, South Africa.

Stoekli, H.F., 1995. Characterization of microporous carbons by adsorption and immersion techniques. In: Patrick, J.W. (Ed.),

S. Girgis, Amina A. Attia, Nady A. Fathy, 299(2007), Colloids and surfaces A: Physico chem. Eng. Aspects

Tan, IAW, Ahmad, AL, & Hameed, BH. (2008b). Preparation of activated carbon from coconut husk: Optimization study on removal of 2, 4, 6-trichlorophenol using response surface methodology. Journal of Hazardous materials, 153(1), 709-717.

Tanaka, H., Takanashi, T. Kadota, M. & Yatazawa, M (1972), Experimental studies on sulfur dioxide injuries in higher plants. — Water. Air. Soil Pollut 1 343-346

Weber, W.J. and B. M. Vliet. (1980). Fundamental concepts for application of activated carbon in water and wastewater treatment.

T. Wigmans. Carbon, 27 (1989) 13, Microporous and Mesoporous Materials.

Ziegler, 1 1973. Effects of sulphite on phosphoenolpyruvate carboxylase and malate formation in extracts of Zea mays. — Phytochemistry 12 1027-1030

Appendix

Appendix A

Raw peanut shell size redaction Impregnation with KOH impregnated dry sample

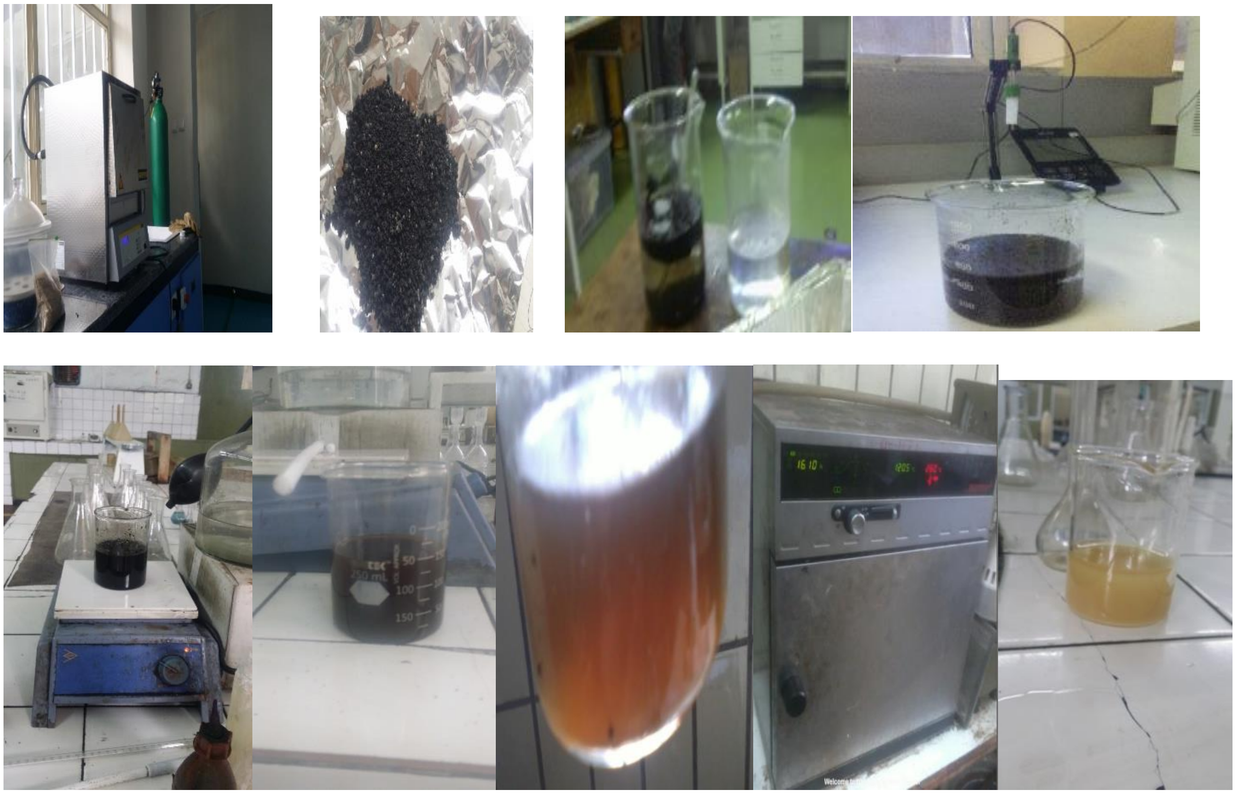
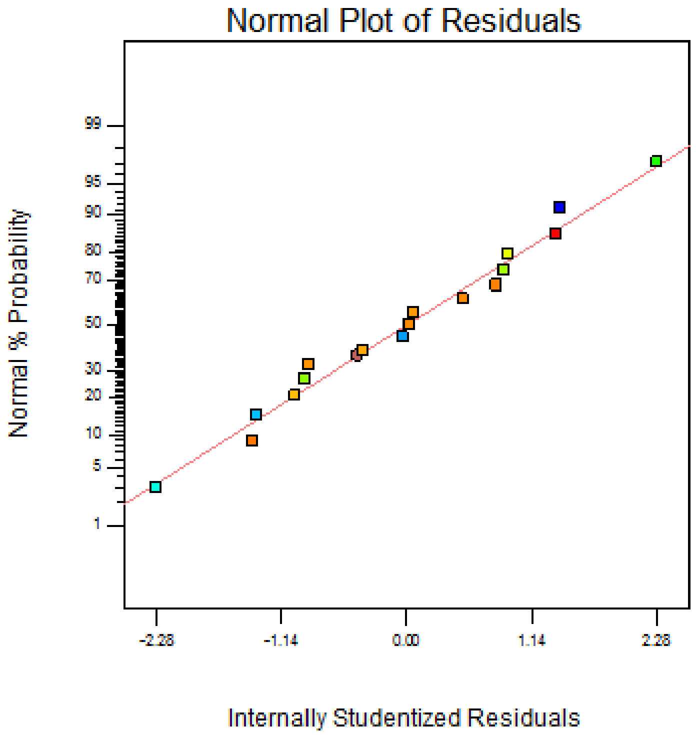
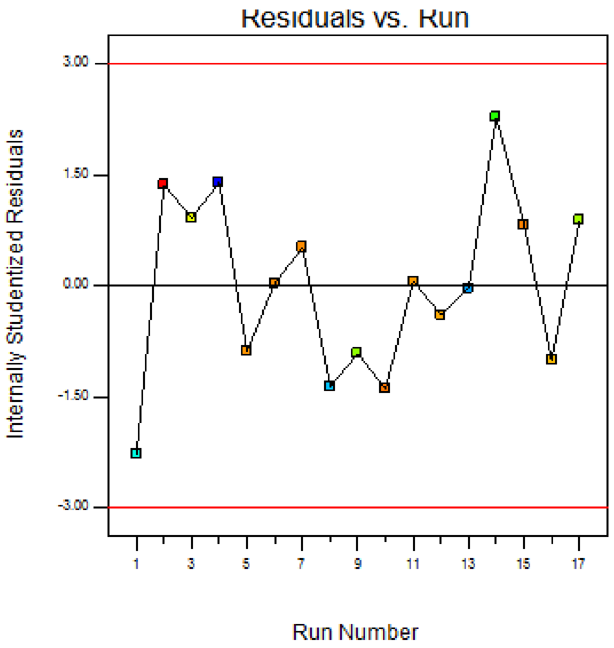


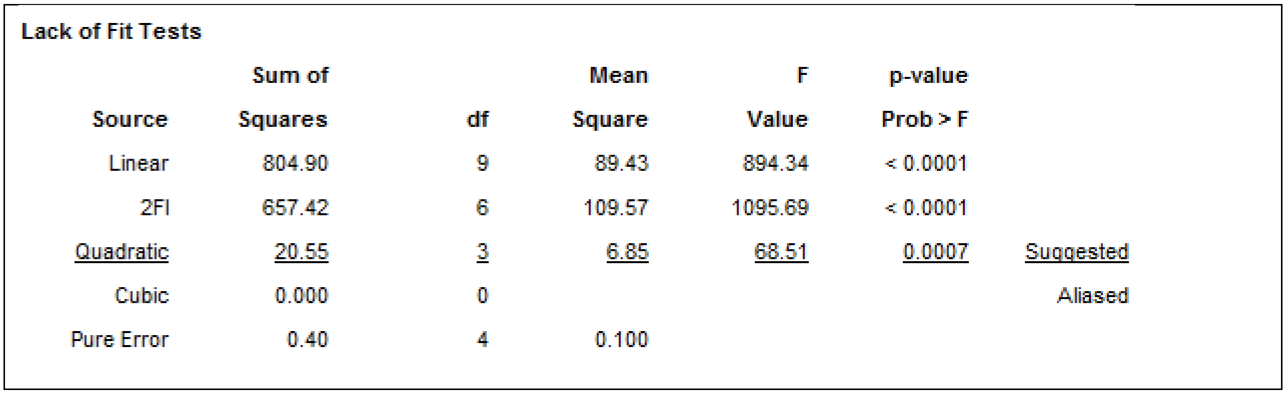
Fig.A1. 1: Sample picture of raw peanut shell, granular activated carbon and adsorption test experiment in laboratory scale.

Appendix B

			Factor 1	Factor 2	Factor 3	Response 1
Std	Run	Block	A:AC-Dosage	B:time	C:temprature	Decolorization efficiency
						%
1	2	Block 1	1	25	45	30.7
2	6	Block 1	3	25	45	61.2
3	8	Block 1	1	75	45	38.3
4	17	Block 1	3	75	45	79.5
5	10	Block 1	1	50	30	36.4
6	9	Block 1	3	50	30	73.9
7	16	Block 1	1	50	60	43.8
8	7	Block 1	3	50	60	79.5
9	14	Block 1	2	25	30	59.7
10	12	Block 1	2	75	30	70.2
11	3	Block 1	2	25	60	61.9
12	1	Block 1	2	75	60	83.8
13	11	Block 1	2	50	45	82.4
14	5	Block 1	2	50	45	80.9
15	15	Block 1	2	50	45	81.8
16	13	Block 1	2	50	45	81.3
17	4	Block 1	2	50	45	82.8

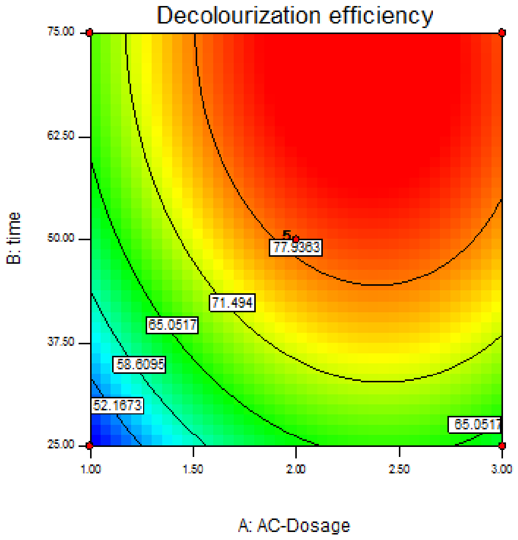

Normal Plot of Residuals
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-2.28
-1.14
0.00
1.14
2.28
Internally Studentized Residuals

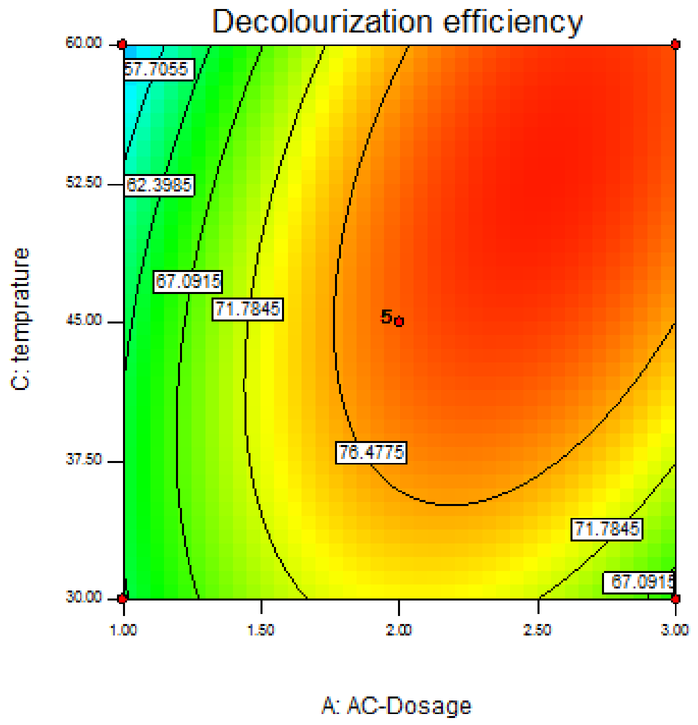

Residuals vs. Run
Internally Studentized Residuals
3.00
1.50
0.00
-1.50
-3.00
1
3
5
7
9
11
13
15
17
Run Number

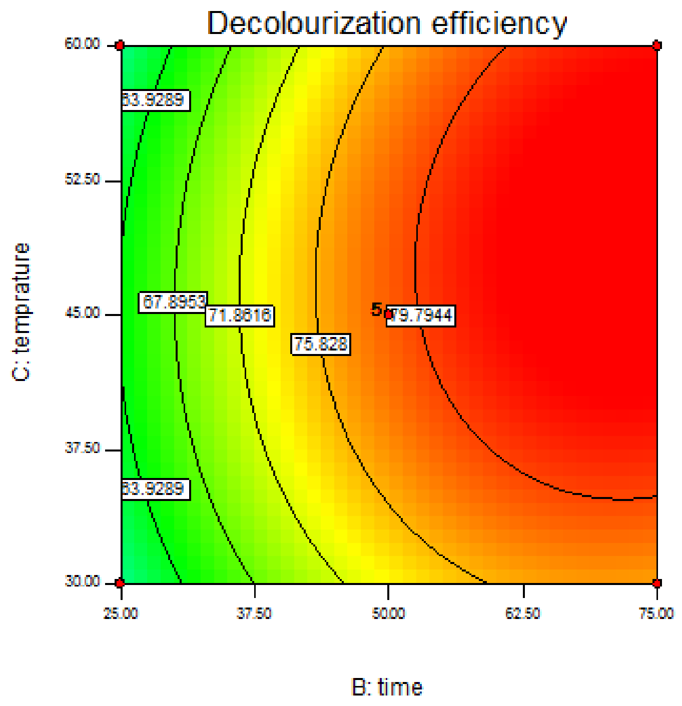


Lack of Fit Tests

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Linear	804.90	9	89.43	894.34	< 0.0001	
2FI	657.42	6	109.57	1095.69	< 0.0001	
Quadratic	20.55	3	6.85	68.51	0.0007	Suggested
Cubic	0.000	0				Aliased
Pure Error	0.40	4	0.100			




Decolourization efficiency
C: temprature
60.00
52.50
45.00
37.50
30.00
A: AC-Dosage
1.00
1.50
2.00
2.50
3.00
57.7055
62.3985
67.0915
71.7845
76.4775
71.7845
67.0915
5


Decolourization efficiency
C: temprature
60.00
52.50
45.00
37.50
30.00
B: time
25.00
37.50
50.00
62.50
75.00
63.9289
67.8953
71.8616
75.828
79.7944
63.9289
5