**ADDIS ABABA UNIVERSITY**

**SCHOOL OF GRADUATE STUDIES**

**SCHOOL OF CHEMICAL AND BIOENGINEERING**

**ENVIRONMENTAL ENGINEERING POST GRADUATE PROGRAM**

# REMOVAL OF GOLDEN YELLOW 28 DYE FROM AQUEOUS SOLUTION USING THERMO-CHEMICAL MODIFIED PEANUT SHELL ACTIVATED CHARCOAL

*A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in Chemical Engineering under Environmental Engineering Stream.*

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**MARCH, 2018**

**ADDIS ABABA, ETHIOPIA**

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIOENGINEERING

Removal of Golden Yellow 28 dyes from aqueous solution using thermo-chemical modified peanut shell activated charcoal

As members of Examining Board of the Final M.Sc. thesis open defense, we certify that we have read and evaluated the thesis prepared by Ashenafi Berhanu, entitled "Removal of Golden Yellow 28 dyes from aqueous solution using thermo-chemical modified peanut shell activated charcoal" and recommended that it can be accepted as fulfilling the thesis requirements for the Degree of Master of Science in Chemical Engineering (Environmental Engineering).

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**Declaration**

I, the undersigned, declare that this thesis entitled "Removal of Golden Yellow 28 dyes from aqueous solution using thermo-chemical modified peanut shell activated charcoal" is my original work, and has not been presented by any other person for an award of a degree in this or any other University, and that all resources of materials used for this thesis have been duly acknowledged.

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Date of submission March, 2018

This thesis has been submitted to the university with my approval as the University Advisor.

Name: Teshome W.(Assistant prof.). _____

## ACKNOWLEDGMENT

First and foremost, I am grateful to the almighty GOD for giving the strength and good health to accomplish this thesis work. Then, I wish to express my sincere thanks and gratitude to my advisor Mr. Teshome W. (Assistant prof.) for his tremendous support and meticulous attention throughout the duration of research and also Dr. Beteley T. for suggesting the research topic.

Special thanks to all the staff in School of Chemical and Bio-Engineering AAiT for their co-operation and help. I would like to put forward my gratitude to our laboratory technicians, especially Mr. Hinetsaselasie, Mr. Aleneh and Mis. Hana, and all the numerous people whose names have not been mentioned. Furthermore, I would also like to thank Ato Eliyas (AAiT PhD candidates in SCBE) and also grateful to the Ato Mesay for the provision of raw peanut shell.

Finally, I also would like to thank my sweet family and my friends for their invaluable help and guidance.

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| PS | Peanut Shell |
| RPS | Raw Peanut Shell |
| AC | Activated carbon |
| Bi-Ch5 | Bio-Char carbon at $500^{o}C$ |
| BM5 | Base Modified carbon at $500^{o}C$ |
| ASTM | American Society for Testing and Materials Standard |
| BET | Brunauer-Emmet-Teller |
| XRD | X-Ray powder diffraction |
| FT-IR | Fourier Transform-Infrared Spectroscopy |
| BOD | Biochemical Oxygen Demand |
| COD | Chemical Oxygen Demand |
| %R | Percentage removal efficiency (%) |
| GY 28 | Golden yellow 28 dye |
| UV/vis | Ultraviolet Visible |

## LIST OF SYMBOLS

| | |
|---|---|
| $C_o$ | Initial adsorbate concentration (ppm) |
| $C_e$ | Equilibrium concentration of adsorbate (ppm) |
| qe | Amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g) |
| qm | Maximum monolayer coverage capacity (mg/g) |
| $R_L$ | Langmuir equilibrium parameter/ separation factor |
| $k_L$ | Langmuir isotherm constant (L/mg) |
| $k_f$ | Freundlich isotherm constant |
| n | Constant of freundlich isotherm |
| $k_1$ | Rate constant of pseudo-first-order sorption Rate |
| $k_2$ | Rate constant of pseudo-second-order sorption |
| $R^2$ | Correlation coefficient |

**ABSTRACT**

In this study, modified activated carbon from agro by-product (peanut shell) has been successfully produced through chemical activation process using sodium hydroxide (NaOH) as an activating agent and also the effect of activation agent and carbonization temperatures on adsorption efficiency, surface characteristics and yield were studied. To produce modified activated carbon, samples were heated to the final carbonization temperatures 400, 500 and 600$^{o}$C respectively under a continuous pure nitrogen flow (99.6%) and at a heating rate of 10$^{o}$C/min with an activation time150min. The physicochemical properties of the raw peanut shell and sodium hydroxide modified peanut shell based activated carbon were characterized by BET, FT-IR, XRD, $pH_{PZC}$ and proximate analysis. The adsorption efficiency tests were performed in the batch adsorption system at different initial concentrations of GY 28 dye 30-150 ppm, contact time 10-90 min, and solution pH 2-10 with 100ml volume of solution at constant solution temperature 25$\pm$5°C and 150rpm with 0.5gm of base modified activated carbon @500$^{o}$C. This modified adsorbent (BM5) removes 83.3% and 25 mg/gm of the GY 28 dye from aqueous solution at optimal pH of 10 and 60 min with fixed amount of adsorbent, 0.5gm. The equilibrium data was analyzed by Freundlich and Langmuir isotherm models. Finally, the rate of the adsorption process was investigated using Pseudo first and Pseudo second order kinetic models. Pseudo second-order kinetic model was found to be well fitted to the data obtained. Based on the Golden Yellow 28 dye removal efficiency test, the activated carbon produce from raw peanut shell by thermo-chemical activation method can be used as one of the alternative adsorbent in dye wastewater treatment.

# 1. INTRODUCTION

## 1.1 Background

Environment contamination, in general and water pollution, in particular has become an increasingly great concern to the community around the world in recent years (Borah *et al*, 2015). Currently, industrial developments have left their impression on the environmental society. Many industries likes textile, paper, printing, carpet, plastic, food processing & cosmetic (Dawood & Sen,2014) rubber, leather tanning and dye manufacturing industries used dyes to color their products and thus produce wastewater containing organics with a strong color, where in the dyeing processes because of the low degree of dye fixation (Adegoke & Solomon, 2015).

Dyes are organic compounds that represent a group of pollutants. It is believed that the dyeing industry is responsible for releasing approximately 100 tons of dyes per year into the environment, contaminating water bodies like rivers and springs (Borah *et al*, 2015; Sharma *et al*, 2014). Of these dyestuffs, 5–15% are lost in industrial effluents & its contaminants causes serious environmental problems and consequently, wastewater treatment is one of the biggest issue and problems we face today (Postai *et al.*, 2016).

The rising existence of dyes in the aqueous bodies is one of the most significant environmental issues. Dyes do not undergo natural degradation; hence the persisting color prevent the passage of light into water bodies and spoils the ecosystem (Kulkarni *et al*, 2017). The presence of dyes in water is undesirable, not only because of their color but also due to their hazardous effects on human health and environment. Some of adverse effects on human health include respiratory sensitization, allergic problems like dermatitis, irritation to eyes, mucous membrane & respiratory tract and also the degraded products are found to be toxic, carcinogenic & mutagenic due to presence of carcinogens and several other aromatic compounds (Manoj *et al*, 2015).

A wide range of methods have been developed for the removal of dyes from water and wastewaters to decrease their impact on the environment specifically on human health but there is no universal and unique method capable of removing dye effluents (Bhatnagar & Sillanpää, 2010). The best choice depends on the types of dyes to be removed, their composition, concentrations and production flow into the water & wastewaters. In the past several years, many technologies & methods have been developed and investigated to find an economic and efficient way

to treat dyeing wastewater or for the removal of dyes from aqueous solutions (Wang *et al*, 2010). The technologies for color removal can be divided into three categories: biological, chemical, physical and combined treatment processes. All of them have advantages and drawbacks (Beyene, 2014; Wang *et al*, 2010).

Most of the dyes are resistant to be decolorized by chemicals, heat, and light due to their complex chemical structures (Ghaedi *et al*., 2012). There are several methods available for color removal from water and wastewaters; every technology has its own some limitations either in the form of ineffectiveness or high cost (Gopal *et al*, 2014). Among these treatment methods, high cost-effectiveness, simple to setup and wide range applicability of adsorption technology opened up new opportunities for the treatment of effluent streams of dying industries (Yener *et al*, 2008).

Adsorption technology has been found to be an efficient and economic process to remove the dyes from the aqueous solutions. Activated carbon has been widely used as an effective adsorbent for the removal of dyes from the aqueous solutions because of their high adsorption capacities and environmental friendly. Although commercial activated carbon is a preferred adsorbent for color removal, its widespread use is restricted due to its relatively high cost of production of activated carbon which led to the researches on alternative non-conventional and low-cost adsorbents (Rafatullah *et al*., 2010). Some of the low-cost adsorbents studied for the removal of dyes from the aqueous solution such as: agricultural by-products like peanut shell, different type of clays, biomass and industrials wastes have gained greater attention due to many obvious advantages such as easy availability, low running cost, comparable efficiency, resource generation, and pollution abatement (Taylor *et al.*, 2015).

In order to improve the adsorption removal efficiency and capacity of the carbon like low cost adsorbents, several modifications have been proposed in the literature. Typically, the modification of activated carbon can be divided into chemical and physical modification (Aworn *et al.*, 2008; Inorgnica, 1992; Paraskeva *et al.*, 2008; Şahin *et al.*, 2016). Chemical modification (Şahin *et al.*, 2016) involves impregnation with chemicals such as $ZnCl_2$, KOH, NaOH, $H_3PO_4$, $H_2O_2$, $HNO_3$, $H_2SO_4$ or $K_2CO_3$ e.t.c followed by heating under a nitrogen,$N_2$ flow at temperature in the range of 450 – 900°C, depending on the impregnate used for this studies IR is 1:1. It is believed that the carbonization step proceeds simultaneously with the chemical activation, and physical activation (Aworn, Thiravetyan, & Nakbanpote, 2008) is a two stage process; it involves carbon-

ization of raw material followed by activation at elevated temperatures (up to 1,100$^{o}$C) in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures. By chemical modification of the biomass surfaces it has become possible to design new, reliable, highly-specified adsorbents, and efficient thickeners of dispersive media. Chemical activation has more advantages over physical activation with respect to higher yield, more surface area and better development of porous structure oxygenated surface complexes in carbon (Malik *et al.*, 2006; Şahin *et al.*, 2016).

Cationic dyes, commonly known as basic dyes, are widely used in acrylic, nylon, silk, wool, and leather dyeing (Marungrueng & Pavasant, 2006; Gupta GS & Shukla SP, 1996). Due to the complex chemical structure of these dyes, they are resistant to breakdown by chemical, physical and biological treatments. Furthermore, any degradation by physical, chemical or biological treatments may produce small amount of toxic and carcinogenic products (Eren & Afsin, 2008). But adsorption is known to be a promising technique, which has great application in the decoloration process. In this work particular GY 28 dye, one of the cationic azo dye is among the most commonly used dyestuff.

## 1.2 Problem of Statements

The removal of dyes from colored effluents, particularly in the dyestuff and textile industries, is one of the major environmental concerns these days. Around 5-15% of dyes used in industry are discharged into the environment, which is harmful to the environment (Postai *et al.,* 2016; Kan-awade *et al.,* 2011). Adsorption is widely used to remove chemical pollutants using adsorbents. Among the most commonly used adsorbent is commercial activated carbon due to adsorption efficiency for all kinds of pollutants. But commercial activated carbon has high cost of production and regeneration which are a constraint for a wide applicability of the process of adsorption (Kharub, 2012). As a result, there is a need to produce low cost and effective adsorbent.

From an economical and environmental point of view, waste to carbon conversion processes is significant (Terrones,2015). The disposal of agro by-product is a current economic and environmental issue. The conversion of these by-products to adsorbent, such as activated carbon, are a research field of interest as it study with the problem of the disposal of agro-residues and producing an added-value product that can be used in environmental applications. In addition, the search for their eco-friendly characteristics, easy availability, low running cost, comparable efficiency, and pollution abatement of these materials have been in focus for wastewater treatment (Demirbas, 2009; Rafatullah, *et al.*, 2010). The most common low cost adsorbents used for the removal of dyes include Nutshells (Wartelle, 2001), peanut hull (Ozer, 2007), rice husk (Lin *et al*., 2013), coconut shell(Aljebore *et al.,(*2014)), bamboo (Guo *et al*., 2014), sawdust (Mane, 2011), bagasse (Mane *et al.*, 2007), types of clays such as bentonite (Eren & Afsin, 2009) & kaolin (Shu *et al.*, 2014), and industrials wastes like fly ash (Ahmaruzzaman, 2010), spent grain (Pedro *et al.*, 2004), red mud (Zhang *et al*, 2014), and sewage sludge (Chu, 2002).

Peanut is an oil plant which is extensively cultured in ethiopia. So it's shell is an abundant and inexpensive agricultural by-product. Most of this by-product is arbitrarily discarded or set on fire. These disposals must result in environmental pollution, So it can be produced an added-value product. Nut's shell and hull have been widely used as adsorbents for the removal of various pollutants from water and wastewaters (Wang *et al.*, 2011). Peanut shell is one of an alternative potential adsorbent materials. So raw or modified peanut shell has been used as an adsorbent in removing dyes (Georgin *et al*., (2016); Honoré *et al*., (2014); Abbas *et al*., (2012); Malik *et*

*al*.,(2006)) and heavy metals (Wang *et al.*,(2011); Witek-Krowiak *et al.*,(2011); Ali, R..(2012); Taşar *et al.*,(2014)) from solutions due to its physiochemical charcteristics.

In many cases, as a cost-effective and non-hazardous alternative to commercial activated carbon, agro by-products or waste served as an adsorbent for removal of dye from wastewaters. However, the adsorption removal efficiency and capacities of raw agricultural by-products tend to be very low. In order to improve the adsorption removal efficiency and capacity of the carbon like low cost adsorbents, several modifications have been proposed in the literature. But, thermo-chemical activation techniques has more advantages over physical activation with respect to higher yield, more surface area and better development of porous structure surface in carbon for better adsorption efficiency (Malik *et al.*, 2006; Şahin *et al.*, 2016). It can be noted that thermo-chemical activation leads to higher surface areas at lower temperatures and has higher yield at shorter retention times than physical activation, hence to lower energy requirements for activated carbon production(Adib *et al.*, 2015). In this study, the removal efficiency of modified peanut shell derived activated carbon using thermo-chemical techniques from a Golden Yellow 28 dye in aqueous solution will be investigated. This may indicate that modify peanut shell will be utilize for dye removal with economic and environmental benefits in industrial wastewater treatment.

## 1.3 Objective

### 1.3.1 General objective

The main objective of this thesis is to study the performance of thermo-chemically modified peanut shell adsorbent for the removal of Golden Yellow 28 dye from aqueous solution.

### 1.3.2 Specific objectives

The specific objective are:-

- To characterize the peanut shell for prepare modified activated carbon
- To prepare and characterize activated carbon from peanut shell using thermo-chemical activation techniques
- To investigate the effect of activation temperature at 400°C, 500°C and 600°C on the surface property of prepared activated carbon respectively.
- To Study the adsorption removal and capacity of basic dye (Golden Yellow 28) from aqueous solutions by chemical modified peanut shell (Base Modified @ 500°C and Bio-Char @ 500°C) in batch process under varying operating condition (contact time, initial dye concentration, and pH)
- To determine the optimal contact time, initial dye concentration and pH for effective dye removal using response surface method
- To study adsorption isotherm and kinetic of the process of behavior

## 1.4 Significance of the Study

Basically, the significance of this study is utilization of agricultural by-product material for new products like modified adsorbent using thermo-chemical techniques rather than land disposal and also the efficiency of this modified adsorbent for the removal of basic dye from aqueous solution for ensuring healthy environment. Beside, this study is also expected to produce a comparable activated carbon meeting the requirements of an effective adsorbent for dye wastewater treatment. If the modified adsorbent performs well in removing color at low cost, they can be used widely in the industrial sector to improve profit and to minimize the cost of this sector. In addition, this work is expected to give an alternative direction towards treatment method of color contaminated water and wastewaters.

## 2. LITERATURE REVIEW

### 2.1 Dye

Dyes are natural and xenobiotic compounds that make the world more beautiful through colored substances. They are basically ionic chemical compounds that can connect themselves to surfaces or fabrics to impart color (Yagub *et al*., 2014); Sharma *et al.,* 2014). Dye molecules comprise of two key components: the chromophores, responsible for producing the color, is a radical configuration consisting of conjugated double bonds (Demirbas, 2009) like azo (–N≡N–), carbonyl (–C=O), methine (–CH=), nitro ($–NO_2$) & quinoid groups and the auxochromes (color helpers), such as carboxylic (-COOH) acid, sulfonic acid ($-SO_3H$), amino ($-NH_3$) and hydroxyl groups (-OH), which can not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity toward the fibers (V K Gupta, 2009; Santos *et al*, 2007).

Dyes exhibit structural diversity and are classified in several ways. it's may be classified, according to chemical constitution, application class and end use (Yagub *et al*., 2014) and on their particle charge up on dissolution & solubility in aqueous application medium see Table 2.1. However, the classification based on application is advantageous before considering chemical structures in detail because of the complexities of the dye nomenclature from this type of system (V K Gupta, 2009). It is also worth to point that classification by application is the principal system adopted by the Color Index (C.I.). In the present study we will try to use the dye names based on their application or their C.I. name/number. This system includes the name of the dye class, its hue, and a number. A five digit C.I. number is assigned to a dye when its chemical structure has been disclosed by the manufacturer. An example of dye basic yellow 28 or Golden yellow 28 is given in Figure 3.2.

Dyes are considered to be particularly dangerous organic compounds for the environment (Taylor *et al*., 2014). Dye wastewater sample contains moderate concentration of chemical oxygen demand (COD), ammonia ($NH_3$) and color (Syafalni, 2012). Synthetic dyes, one group of organic pollutants, are extensively used in several industries such as textile, paper, leather, printing and dye stuff houses. The effluents of these industries are highly colored (Aksu, 2005) and discharge of dye containing effluents into the natural water bodies can pose hazardous effects on the living systems because of carcinogenic, mutagenic, allergenic and toxic nature of dyes (Yagub *et al.,* 2014). The presence of very small amounts of dyes in water ($\leq$ 1 ppm for some

dyes) is highly visible and undesirable. Dye effluents can cause several problems: dyes can have acute or chronic effects on exposed organisms, which depends on exposure time and dye concentration; and the dyes' absorption and reflection of sunlight entering the water can interfere with the growth of bacteria to levels sufficient to biologically degrade impurities in the water and start the food chain.

Cationic dyes like C.I. BY 28 or GY 28 , generally known as basic dyes and included in a complex dye family and used in acrylic, leather, silk, wool and nylon dyeing (Marungrueng & Pavasant 2006). The release of azo dyes into the environment is a concern due to not only the property coloring natural waters but also harmfulness (toxicity, mutagenicity, and carcinogenicity) of these dyes and their bio-transformation products (Gupta *et al*., 2007). In particular, GY 28, one of the cationic azo dye, studied in this work is among the most commonly used dyestuff to dye cotton and polyacrylonitrile and therefore a common industrial pollutant (Köneço *et al.*, 2015).

Table 2.1 Classification of dyes (V K Gupta, 2009; Santos *et a.l*, 2007).

| Classification of dyes based on | Grouped | Dyes |
|---|---|---|
| Use | Dying in processes | Acid dyes, basic dyes, direct dyes, mordant dyes, vat dyes, reactive dyes, disperse dyes, azo dyes, and sulfur dyes |
| Solubility | Soluble | Acid, Mordant, Metal complex, Direct, Basic and Reactive dyes |
| | Non-soluble | Azoic, Sulfur, Vat and Disperse |
| Chemical structure | Azo linkage | |
| | Anthraquinone unit | |
| Charge dissolution | Cationic | All basic dyes |
| | Anionic | Direct, Acid, and Reactive dyes |
| | Non-ionic | Dispersed dyes |

## 2.2 Treatment Technologies for Dye Removal from Wastewaters / Aqueous Solution

Most of industries wastewaters have a large amount of complex components with high concentrations of organic, high colored and changing greatly characteristics. Owing to their high BOD/COD, their coloration and their salt load, the wastewater resulting from dyeing stuff with basic dyes are seriously polluted. As aquatic organisms need light in order to develop, if any deficit in this respect caused by colored water leads to an imbalance of the ecosystem. Moreover, the water of rivers, springs, oceans and any other water bodies that are used for drinking water, irrigation or for other purpose must not be colored even if disposes into it, otherwise the treatment costs will be increased (C.All`egre *et al.*,2006). Obviously, large numbers of published literature studies concerning the feasibility of treating dyeing wastewater are very important.

Therefore, Currently many researchers have been studied the effectiveness of dyes removal from aqueous solution by different separation methods. However, due to the variety of existent dyes and the effluents complexity, not all methods have the same efficiency and each method has its limitations based on running cost, removal efficiency, design and operation efficiency (Dawood & Sen, 2014; Ferreira *et al*., 2014). Generally, the treatment methods can be gruoped into three main categories namely physical, chemical and biological methods and hybrid treatment processes (Ghoreishi & Haghighi, 2003; Holkar *et al.*, 2016). All of these methods have their own advantages and disadvantages see Table 2.2.

### 2.2.1 Biological methods

Biological treatment is the most economical methods compared to physical and chemical methods that why it is the most common and widespread technique used in dye wastewater treatment (Costa *et al.*, 2007). The biological process removes only the dissolved matter in wastewaters. The removal efficiency is influenced by the ratio of organic load/dye and the microorganism load, its temperature, and oxygen concentration in the system. The principle of the biological treatment procedures is the conversion of biodegradable wastes into simpler and harmless species through biological processes by various microorganisms. A large number of micoorganisisms have been used for decolouration and mineralization of various dyes such as bacteria, yeasts, algaes and fungi (Gupta V & Suhas 2009). The methodology offers considerable advantages like being cost-competitive ( relatively inexpensive & having low running costs) and the end products of complete mineralization not being toxic eco-friendly nature, minimum usage

of chemicals and energy saving nature. So biological treatments are suitable for variety of dyes, but the main drawbacks of the biological treatment is low biodegradability of the dyes, less flexibility in design & operation, larger land area requirement and longer times required for decolourisation processes thereby making it incapable of removing dyes from effluent on a continuous basis in liquid state fermentations (Beyene, 2014; Crini, 2006). On the basis of oxygen requirement, the process can be aerobic (in presence of oxygen), anaerobic (without oxygen) or combined aerobic–anaerobic (Costa *et al.*, 2007).

**Combined aerobic–anaerobic treatment**

Currently, in order to get better remediation of colored compounds from the dying industrie's effluents, a combination of aerobic and anaerobic treatment is suggested to give encouraging results. An advantage of such system is the complete mineralization which is often achieved due to the synergistic action of different organisms. Also, the reduction of the azo bond can be achieved under the reducing conditions in anaerobic bioreactors and the resulting colorless aromatic amines may be mineralized under aerobic conditions, thereby making the combined anaerobic–aerobic azo dye treatment system attractive. Thus an anaerobic decolourization followed by aerobic post- treatment is generally recommended for treating dye wastewaters (Gupta V & Suhas 2009). However, conventional biological processes are not effective for treating dyestuff wastewater because many commercial dyestuffs are toxic to organism being used and result in the problems of sludge bulking, rising sludge and pin flock, and most dyes are designed to resist to microbial (Kharub, 2012).

### 2.2.2 Chemical treatment methods

Chemical operations, as the name suggests, are those in which strictly chemical reactions occur, such as precipitation. Chemical treatment relies upon the chemical interactions of the contaminants we wish to remove from water, and the application of chemicals that either aid in the separation of contaminants from water, or assist in the destruction or neutralization of harmful effects associated with contaminants (Z. Wang *et al.*, 2010).

Chemical methods including coagulation or flocculation combined with flotation and filtration, chemical precipitation-flocculation with Fe (II)/Ca $(OH)_2$ called Fenton reaction, electro flotation, conventional oxidation methods by oxidizing agents (ozone) called ozone oxidation, or electrochemical processes and the new method one AOP. Chemical treatment methods are

applied both as stand-alone technologies and as an integral part of the treatment process with physical methods. Dyes can be removed completely by chemical techniques but it is an expensive, and accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use (J. G. mantano *et al.*, 2007). Currentlly, AOP, Fenton oxidation and ozone oxidation are often used in the wastewater treatment for dye removal.

**Advanced oxidation process (AOP)**

Recently, the emerging techniques, known as AOP, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive (Beyene, 2014). The most frequently utilized AOPs uses $H_2O_2$, dissolved oxygen as their oxidant. Amongst AOPs, the combination of (ultra violet / $Ti_2O$/ $H_2O_2$) and (ultra violet / $H_2O_2$) are acknowledged as the most guaranteeing for the remediation of polluted waters. The high electrical energy demand and the consumption of chemical reagents are also common problems (Aiyer *et al.*, 2015).

**2.2.3 Physical treatment methods**

A conventional treatment process is comprised of a series of individual unit processes, with the output (or effluent) of one process becoming the input (influent) of the next process. The first stage will usually be made up of physical processes. Physical wastewater treatment has been widely used in the sewage treatment plant which has a high removal of dissolved and suspended substances, while it has a low removal of COD (Z. Wang *et al.*, 2010). Different physical methods are also widely used, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis, ...), ion exchange mehodes, and adsorption techniques (Dawood & Sen, 2014).

## Membrane separation

Membrane separation process is the method that uses the membrane's micropores to filter and makes use of membrane's selective permeability to separate certain substances in wastewater. Currently, the membrane separation process is often used for treatment of dyeing wastewater mainly based on membrane pressure, such as reverse osmosis, ultrafiltration, nanofiltration and microfiltration. This separation process is a new separation technology, with high separation efficiency, low energy consumption, easy operation, no pollution and so on. However, this technology is still not large-scale promoted because it has main drawbacks the high investment costs, the limitation of requiring special equipment, limited lifetime, and also during the operation of treatment various suspended particles such as dyes and organic matter tend to accumulate within a thin boundary layer the membrane surface & result in potential membrane fouling, and the production of a concentrated dyebath which needs to be treated (Holkar *et al.*, 2016; Santos *et al.*, 2007).

Various processes have been investigated for treatment of dye effluents. Among all treatment processes, the adsorptive process is a sludge free process, low energy and chemical requirements, and using as a sorbent is found to be effective in removal of dye and is firmly established as most reliable one (A. Gupta & Balomajumder, 2015). Adsorption is also known to be a promising technique, which has great importance due to the ease of operation and comparable low cost of application in the decoloration process.

Table 2.2 Advantages and disadvantege of treatment methods (Salleh *et al.*,, 2011; V K Gupta, 2009; Crini, 2006 )

| Separation Technique | Advantages | Disadvantages |
|---|---|---|
| **Physiochemical** | | |
| Adsorption | High adsorption capacity for all dyes | High cost of adsorbents<br>Need to dispose of adsorbent<br>Low surface area for some adsorbents |
| Ion exchange | No loss of sorbents | Not effective for dispose dyes |
| Membrane filtration | Effective for all dyes with high quality effluent | Suitable for treating low volume and production of sludge |
| Electro-kinetic coagulation | Economically feasible | Need further treatments by flocculation and filtration and production sludge |
| **Chemical** | | |
| Fenton reagent | Effective process and cheap reagent | Sludge production and disposal problem |
| Ozonation | No production of sludge | Half-life is very short (20 minute) and high operation cost |
| Photo-catalyst | Economically feasible and low operational cost | Degrade of some photo-catalyst into toxic by products |
| **Biological** | | |
| Aerobic degradation | Efficient in the removal of azo dyes and low operational cost | Very slow process and provide suitable environment for growth of microorganisms |
| Anaerobic degradation | By products can be used as energy sources | Need further treatment under aerobic conditions and yield of methane and hydrogen sulfide |

## 2.3 Adsorption

Adsorption is a surface phenomenon in which adsorbate molecules or ions (liquid or gas) are concentrated on the surface of a solid. It is a process of binding molecules or particles onto the external surface of solid or internal surface, if the material is porous in a very thin layer (Dabrowski,2001;A. Gupta & Balomajumder, 2015). Adsorption is an effective alternative process for the treatment of contaminated wastewater for color removal based on the high affinity of many dyes for adsorbent materials (Tunali *et al.*, 2009).

### 2.3.1 Principle of adsorption

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The process can take place in any of the following systems: liquid-gas, liquid-liquid, solid-liquid and solid-gas. The adsorbing phase is the 'adsorbent', and the material concentrated or adsorbed at the surface of adsorbing phase is the 'adsorbate'(Kandasamy *et al*., 2006). Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. In case of water treatment, the process occurs at an interface between solid adsorbent and contaminated water. Separation occurs because of differences in molecular weight, shape or polarity, causes some molecules to be held more strongly on the surface than others. In many cases, the adsorbate is held strongly enough to allow complete removal of that component from the fluid (Ali *et al*., 2012). In the adsorption process, dye molecules may be adsorbed on the surface of an adsorbent through several forces such as van der Waals forces, hydrogen bonding, electrostatic force of interactions, hydrophobic interactions and chemical prosses. Adsorption occurs in three steps. First step, the adsorbate diffuses from the major body of the stream to the external surface of the adsorbent particle. Second step, the adsorbate migrates from the relatively small area of the external surface to the pores within each adsorbent particle. The bulk of adsorption usually occurs in these pores because there is the majority of available surface area. Final step, the contaminant molecule adheres to the surface in the pores (Beyene, 2014). When using AC, the adsorption process results from interactions between the carbon surface and the adsorbate. These interactions can be electrostatic or non-electrostatic.Generally, adsorption process is classified as physisorption and chemisorption.

***Physisorption***:- a type of adsorption in which the forces of attraction are intermolecular forces (van der Waals forces, hydrogen and dipole - dipole) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors, and do not involve a significant change in the electronic orbital patterns of the species involved. The adsorbed molecules are not fixed to a specific site at the surface of adsorbent but are free to undergo translational movement within the interface. It is predominant at low temperature and is characterized by relatively low energy of adsorption. In the majority of cases physical adsorption is easily reversible (Koumanova *et al.*, 2005; Yagub *et al.*, 2014).

***Chemisorption***:- is adsorption in which the forces involved are forces of the same kind as those operating in the formation of chemical compounds. Generally, adsorbents possess porous structures to increase the total exposed surface area and allow fluid to pass through faster. Chemical adsorption occurs when strong interparticle bonds are present between the adsorbate and adsorbent due to an exchange of electrons. Examples of such bonds are covalent and ionic bonds. Chemisorption is deemed to be irreversible in the majority of cases (Koumanova *et al*., 2005; Yagub *et al*., 2014).

### 2.3.2 Factors affecting adsorption process

Adsorption techniques for wastewater treatment have become more popular in recent years. As stated in variruos studies; factors such as pH, temperature, particle size, initial dye concentration and adsorbent mass can influence the rate and extent of dye uptake or that govern the performance of most of the adsorption process but ont only such factors. Adsorption can produce high quality water while also being a process that is economically feasible. Decolourisation is a result of two mechanisms adsorption and ion exchange, and is influenced by many factors including dye/sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time. Optimization of such conditions will greatly help in the development of industrial-scale dye removal treatment process (Koumanova, Allen, & Koumanova, 2005). Some of the factors affecting adsorption of dyes are discussed below;

#### 2.3.2.1 The effect of pH on adsorption

The efficiency of adsorption is dependent on the solution pH, since variation in pH leads to the variation in the degree of ionization of the adsorptive molecule and the surface properties of adsorbent (Yagub *et al.*, 2014). Any oxide surface creates a charge (+ ve or - ve) on its surface.

This charge is proportional to the pH of the solution which surrounds the oxide particles(Koumanova *et al.*, 2005). pH value of the solution will determine the surface charge of the adsorbent which will affect the interaction between the adsorbate and adsorbent. There are two possible mechanisms for the effect of pH on adsorption of dyes on any adsorbent: electrostatic interaction between the protonated or deprotonated groups of adsorbents with dyes, and the chemical reaction between the adsorbate and the adsorbent. The $H^+$ and $OH^-$ are adsorbed quite strongly, and therefore, the adsorption of other ions is affected by the pH of the solution. The change of pH affects the adsorptive process through dissociation of functional groups on the active sites of the adsorbent. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of the adsorption process. It is a common observation that the surface adsorbs anions favorably at lower pH due to presence of $H^+$ ions, whereas, the surface is active for the adsorption of cations at higher pH due to the deposition of $OH^-$ ions. The pH value of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity.

### 2.3.2.2 Effect of contact time on adsorption

The contact time between the pollutant and the adsorbent is significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficiency of that adsorbent for its use in wastewater treatment. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

### 2.3.2.3 Effect of initial concentration on adsorption

The dye concentration also plays an important role in the adsorption capacity of adsorbents. The effects of initial dye concentration are useful in understanding the adsorption kinetics of a pro-

cess. It is usually measured when the amount of dye adsorbed on the adsorbent is in a state of dynamic equilibrium with the amount of dye desorbing from the adsorbent. The adsorption percentages of dyes are inversely related to the initial dye concentration. The adsorption sites absorbed the available solute more quickly at low concentrations. This result may be attributed to the lack of available active sites required for the high initial concentration of the dyes (Djilani *et al.*, 2015).

### 2.3.3 Types of adsorbents

Adsorption is recognized as one of the most effective process used in developing countries and currently being used extensively for the removal of organic pollutants like dye from the aqueous media and real wastewaters (Anastopoulos & Kyzas, 2014; Gupta *et al*., 2013) for advanced wastewater treatment. Many of works have been recently published with primary goal in the investigation of removal of different pollutants (either in gas or liquid medium) using adsorbent materials. Cost of adsorbent, high affinity of the adsorbent for the adsorbate species and adsorbent regeneration ability are the main characteristics which need to be considered during the selection and comparsion of an adsorbent for color removal(Grace *et al.*, 2009; Holkar *et al.*, 2016)

Different types of adsorbents are classified into natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities. Synthetic adsorbents are adsorbents prepared from agricultural byproducts and wastes, household wastes, industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Different commercial activated carbon is a preferred sorbent for color removal, but it is not widely used because of high cost and low regeneration of activated carbon (Kharub, 2012).

Recently several researchers investigated the dyes adsorption ability on a large variety of low cost non-conventional adsorbents such as, agricultural byproduct & waste, industrial waste, sewage sludge, natural material and bio sorbent (Rafatullah *et al.*, 2010). However, non-conventional adsorbents showed mixed results and in very few cases the adsorption capacity of these low cost adsorbents is higher than activated carbons. Therefore, the search to develop

efficient adsorbents having the higher adsorption capacity and better regeneration capacity is still going on (A. Gupta & Balomajumder, 2015; Vinod Kumar Gupta *et al.*, 2013). The removal of dyes from water and wastewater are generally carried out by adsorption using activated carbon, low cost adsorbents and other types of adsorbents (Rafatullah *et al.*, 2010).

### 2.4 Activated Carbon

Industries engaged in dyeing operation generate colored effluent due to the presence of spent dyes. Adsorption is one of the most effective and compareble low cost method among the various treatment processes for removal of dyes from effluents (Hameed & Rahman, 2008). Activated carbon is mostly used as an adsorbent in the treatment process. Attempts have been made by researchers to use non-conventional, low-cost, naturally-occurring biomass as adsorbents, including agricultural byproducts & waste, household waste, and industrial waste (Demirbas, 2009).

In addition, the search for eco-friendly materials for water and wastewater treatment with low cost, and with non-hazardous by-products/wastes generation have been in focus. In this perspective, use of natural bio-based materials has gained wide attention in recent years due to their eco-friendly characteristics, low cost, high uptake capacity, less sludge generation, possible regeneration and availability of these materials in abundance (Demirbas, 2009; Rafatullah, Sulaiman *et al.*, 2010).

The term AC is basically referred as carbonaceous materials, with high porosity, high physicochemical stability, high adsorptive capacity, high mechanical strength, high degree of surface reactivity, with immense surface area which can be differentiated from elemental carbon by the oxidation of the carbon atoms that found at the outer and inner surfaces (Adib *et al*, 2015). AC, also called activated charcoal or activated coal and sometimes called as solid sponge, is a form of carbon that has a structurally homogeneous material of high surface area (up to 3000 $m^2$ $g^{-1}$), has microporous structure and show radiation stability available for adsorption or chemical reactions (Iqbal & Ashiq, 2007; Mahmoudi *et al.*, 2014). The excellent adsorption abilities and economic promise of activated carbons can be attributed to their origin from natural materials such as biomass, lignite and coal, which exhibit high sorption properties (Rafatullah *et al.*, 2010).

Activated carbon has been popular choice as an adsorbent for the removal of various dyes but commercial activated carbon is a preferred sorbent for color removal, its widespread use is restricted due to high cost its poses an economical problem(Dias *et al.*, 2007). Therefore, there is a need for the development of low cost and easily available materials, which can be used more economically on large scale ( Crini, 2006, Rafatullah *et al.*, 2010; Salleh *et al.*, 2011).

### 2.4.1 Non Convetional Low Cost Adsorbent For Dye Removal

Conventional activated carbon is used for the removal of a variety of pollutants from waste waters. In spite of that, there is a major disadvantage associated with it to regenerate the activated carbon, due to its high cost, to allow for further use, thus imparting additional costs to the adsorption process. Many non-conventional low-cost adsorbents, including natural materials, bio-sorbents and waste materials from house, industry and agriculture can be used as inexpensive precursors with high carbon and low inorganic content.

Low-cost adsorbents are materials that basically require little processing and abundant in nature, or are by-products or waste materials from other processes. Agricultural by-products are available in large quantities and constitute one of the most abundant renewable resources in the world. A low raw material cost as wastes are being utilized, abundant availability since the wastes are being produced in large quantities daily & sustainability due to utilization of renewable resources. The uses of activated carbon derived from agricultural residues in many fields were evidently proven in this review (Ahmad *et al.*, 2015; Mahmoudi *et al.*, 2014; Rafatullah *et al.*, 2010; Demirbas, 2009; Crini, 2006). Activated carbon can be produced by both naturally occurring and synthetic of carbonaceous solid precursor. The type and structure of starting materials see Table 2.3 or precursor plays a major role in influencing the quality, characteristics and properties of the resulting activated carbon. And in addition, the properties of the resulting activated carbon will also be influenced by types of activating reagents, time, impregnation condition, carbonization temperature, and inorganic impurities.

Some of the low-cost adsorbents studied for the removal of dyes from the aqueous solution such as: agricultural by-products like Nutshells (Wartelle & Marshall, 2001), peanut hull (Ozer & Ozer, 2007), rice husk (Lin *et al.*, 2013), Rice Husk Ash & Neem leaves (Rana & Singh, 2014), coconut shell, bamboo (Guo *et al*., 2014), sawdust (Mane & Babu, 2011), sugar cane bagasse & bagasse fly ash (Mane *et al.*, 2007), different types of clays such as bentonite (Eren & Afsin,

2009) & kaolinite (Shu *et al.,* 2014), and industrials wastes like fly ash (Ahmaruzzaman, 2010), red mud (Zhang *et al*, 2014), moringa oleifera seed press cake (Tie *et al.*. 2015), sewage sludge and activate sludge (Chu & Chen, 2002) and biomass have gained greater attention due to many obvious advantages such as easy availability, low running cost, comparable efficiency, resource generation, and pollution abatement (Taylor *et al.*. 2015).

Table 2.3 Characteristics of various raw materials used for making AC (Sulyman *et al*., 2017)

| **Raw material** | **Carbon ( %)** | **Volatile ( %)** | **Density Kg/m$^3$** | **Ash (%)** | **Texture of AC** |
|---|---|---|---|---|---|
| Softwood | 40 - 45 | 55 - 60 | 0.4 – 0.5 | 0.3 – 1.1 | Soft, large pore volume |
| Hardwood | 40 - 42 | 55 - 60 | 0.55 – 0.8 | 0.3 – 1.2 | Soft, large pore volume |
| Lignin | 35 - 40 | 58 - 60 | 0.3 – 0.4 | - | Soft, large pore volume |
| Nut shells | 40 - 45 | 55 - 60 | 1.4 | 0.5 – 0.6 | Hard, large multi pore volume |
| Lignite | 55 - 70 | 25 - 40 | 1.0 – 1.35 | 5 - 6 | Hard small pore |
| Soft coal | 65 - 80 | 25 - 40 | 1.25 – 1.50 | 2.12 | Medium hard medium and micro-pore volume |
| Petroleum coke | 70 - 85 | 15 - 20 | 1.35 | 0.5 – 0.7 | Medium hard medium and micro-pore volume |
| Semi hard coal | 70 -75 | 1 – 15 | 1.45 | 5 - 15 | Hard large pore volume |
| Hard coal | 85 - 95 | 5 - 10 | 1.5 – 2.0 | 2.15 | Hard large volume |

### 2.4.2 Type of Activated Carbon Preparation

Any inexpensive material that has a high carbon and a low inorganic content can be utilized as a precursor for activated carbon productions. The preparation of activated carbon from agricultural by-products/ lignocellulosic materials by physical or chemical activation is very important from the industrial point of view. The type and degree of activation could affect the physical and chemical properties of the activated carbon. The purpose of activation is basically to develop fur-ther porosity and creating some ordering of the structure which results in a highly porous solid of

the activated carbon. Both activations are responsible in varying the structure/ shapes and the sizes of AC (Adib *et al.*, 2015; Abioye & Nasir, 2015; Karago, 2008 ).

### 2.4.2.1 Physical Activation

This is usually a two-stage process i.e. carbonization and activation. The first stage involves carbonization of the material at high temperatures (400-850$^{o}$C) under an inert atmosphere ($N_2$, Ar). During this stage the material decomposes into three fractions: chars, tars and gases. Carbonization is a process of obtaining charcoal from the starting material. The resulting charcoal has a low surface area and is very low an active product; the purpose of the carbonization is to reduce the volatile content of the starting material to convert the resulting char with higher content of fixed carbon for activation purpose. In activated carbon production the heating is usually at medium temperatures and slow heating rates, as the preference is that the fraction of char should be maximized. This is followed by the actual activation stage where the charred material comes into contact with the activating agent (steam, $CO_2$, air or mixture of its) under heating and for a specific retention time. During this process chemical reactions between the char and the activating agent lead to the formation of meso and micropores, which form the porous structure of the activated carbon. During the pyrolysis and activation processes the parameters to monitor are temperature, heating rate, retention time and activating agent. Carbonization temperature usually ranges between 400 & 850$^{o}$C and activation temperature generally around 600–1100$^{o}$C (Adib *et al.*, 2015; Rafatullah *et al.*, 2010 ).

### 2.4.2.2 Chemical Activation

In chemical activation a chemical agent is used prior to activation. The commonly used chemicals include $H_2SO_4$,$H_3PO_4$, KOH, NaOH and $ZnCl_2$. The processes involve impregnation of the material with the chosen chemical in solid or liquid form. Such impregnation can take up to 24 hr depending on the chemical used, the precursor and the subsequent processes. Apart from temperature and retention time, the ratio of chemical to precursor is of paramount importance. A washing step of the material is also involved either with distilled water or a mild acid, to remove residual chemicals from the material. By chemical modification of the oxide surfaces it has become possible to design new, reliable, highly specified adsorbents, selective catalysts, polymer extenders, thickeners of dispersive media (Dabrowski, & V.A.Tertykh,editors, 1996).

Chemical activation with sodium hydroxide or potassium hydroxide gives highly porous ACs with consequently high surface areas. Many researchers (Hassan & Youssef, 2014) have recently studied the preparation of ACs with sodium hydroxide and potassium hydroxide starting with different precursors and produced ACs with surface areas from 500 upto 2875 $m^2/g$, total pore volume of about 0.84-2.18 mL/g, and pore radius around 1.382 nm.

Comparing chemical and physical activation processes based on surface areas, yield, pore size and volume, rentention time, and energy consmption (B.O. Ogunsile *et al*,.2014). It can be noted that chemical activation leads to higher surface areas at lower temperatures and has higher yield at shorter retention times than physical activation, hence to lower energy requirements for activated carbon production and only involves one step, creates well developed micro porosities, and reduction of mineral matter content as compared to the physical activation(Adib *et al*., 2015). As mentioned earlier the ratios of chemical material in the literature were in the range 0.25:1 to 4:1 w/w. Such ratios involved the consumption of quite large amounts of chemicals, with respect to the starting material, which in turn, would cause an additional cost to the production process. The vast majority of the studies examined were performed on a laboratory scale and data regarding cost estimates and cost analysis of the end product were not available (Rafatullah *et al*., 2010). However, there are also some disadvantages in chemical activation such as washing is needed to remove the impurities that coming from the activating agents and also the corrosiveness properties of the agents (Adib *et al*., 2015).

### 2.4.3 Factors For The Preparation Of Activated Carbon From Low Cost Adsorbent

The effects of various parameters on the preparation of activated carbon such as carbonization & activation temperature, time, types of activating agents and impregnation ratio. Various physical and chemical processes for the activation of the agricultural residues have their effects on the textural properties such as surface area and pore volume (Adib *et al*., 2015).

In general, preparation of activated carbon is commonly classified into chemical and physical activation. Since chemical activation usually takes place at a lower temperature and a shorter time is needed for activating the materials, the chemical activation is lower energy cost. The most studied chemical activation parameters are time, temperature and IR. The activation time has little influence on the process (1 and 2 hr are common in most works). In contrast, activation temperature and IR are very important. Generally, the increase in activation temperature leads to

an increase in surface area and a decrease in yield. The IR shows a similar behavior; however, the yield decrease is less pronounced and larger surface areas are obtained.

**Effect of Temperature on Surface Area and Pore Volume AC**

A high surface area, a pore size distribution and the nature & the amount of the surface functional groups (the presence of heteroatoms such as H, $O_2$, $N_3$ etc. and inorganic ash) existing in the activated carbon surface are very important for the activated carbon to perform well in a particular application like adsorption (Mahmoudi, Hamdi, & Srasra, 2014).

Carbonization and the activation temperatures affects the activated carbon produced, followed by heating rate, nitrogen flow rate and carbonization time. The activation temperatures play an important role in determining the porous structure, the surface area and the yeild of activated carbon. Activation temperature determines the devolatilisation, activation reaction rates of the carbon and also affect the quality of activated carbon from agriculture byproducts. It is known that theoretically the function of the total surface area and pore volume will increase and then decrease with temperature. Since at the increase of temperature will allow better micropore development and results in larger surface areas and pore volume but also it leads to a decreased of the solid yield and an increased of the liquid and gases; that why in our case to specified the activation tempratures 400, 500 & 600$^{o}$C. Many researchers have linked the surface area and total pore volume of the activated carbon with the degree of burn-off. They suggested that the activation time produced a positive effect on the BET surface area as more porosity was developed in the carbon. Generally, the more increased of the temperature would increase the ash and fixed carbon percentage and decrease the volatile matter respectively ( Adib *et al.*, 2015; Mahmoudi *et al.*, 2014 ).

## 2.5 Raw Peanut Shells

Biomass is one of the most promising renewable energy resources. The peanut, or groundnut (Arachis hypogaea), is a species in the legume "bean" family. The world production of 34.43 million metric tons has been reported in 2008–2009. China and India are the world's largest producers of peanuts and the yield of peanut shell is abundant annually; therefore, it is worthy to convert peanut shell into high-value material through thermochemical methods such as pyrolysis. In particular, potassium has a marked influence on the pyrolysis behavior of biomass, modifying both the yield and distribution of reaction product so peanut shell has a high content of mineral matter, especially K ( X.Wang *et al.,* 2011). Peanut/groundnut's shell (husk)/hull have been widely used as adsorbents for the removal of various pollutants from water and wastewaters. Peanut is an oil plant which is extensively cultured in ethiopia. So it is an abundant and inexpensive agricultural by-product. Most of this agricultural by-product is arbitrarily discarded or set on fire. These disposals must result in environmental pollution. So natural peanut shell or modified peanut shell has been used as an adsorbent in removing dyes and heavy metals from solutions. Peanut shell, mainly consisted of polysaccharides, proteins, and lipids, offer manypolar functional groups such as carboxyl, carbonyl, hydroxyl and amino which can be involved in metal and dye binding (Song *et a*l., 2011). Peanut shell is one of the potential adsorbent materials see figure 3.1. It can be utilized for dye removal as it can also bring unlimited number of economic and environmental benefits to the industrial wastewater treatment.

Sana Sadaf and Haq Nawaz Bhatti were investigated the adsorption potential of peanut husk biomass in batch and continuous mode study in 2014. Experiments were conducted to compare the adsorption capacity of native (raw), acetic acid treated and immobilized peanut husk biomass. Characterization of adsorbent was carried out by SEM and FT-IR. Maximum Indosol Yellow BG dye removal; 79.7 mg/g and 25.9 mg/g were obtained with acetic acid treated peanut husk biomass at pH 2 with with 0.05 g/50 mL biosorbent dose. Fixed bed study was carried out to optimize bed height, flow rate and initial dye concentration. Based on FT-IR analysis showed the involvement of hydroxyl, carbonyl and carboxyl groups in the adsorption process with high adsorption potential. So this biomass can be used for the treatment of of dye containing waste water (Sadaf & Bhatti, 2014).

Color removal has been done using peanut shell obtained from a local farm at Santa Maria-RS in Brazil. AC samples were prepared from peanut shell by pyrolysis; P and microwave irradiation followed by pyrolysis; MW-P. These samples and raw peanut shell were characterized by BET, FTIR and SEM, being applied to remove organic dye like Direct Black 38 and Reactive Red 141 dyes from aqueous solutions. It evaluated the performance of adsorption process, by pH effect, kinetic, equilibrium and desorption studies. From experimental work, MW-P sample showes superior characteristics such as texture, surface area, pore volume, pore size and also adsorption capacity were 110.6 and 284.5 $mgg^{-1}$ respectively; at pH 2.5 than the other two. The adsorbent reuse is possible for two times. The results revealed that the MW-P is a treatment process more adequate to prepare an AC with interesting characteristics for purpose of dyes removal (Georgin *et al.*, 2016).

The metal ion adsorption efficiencies of the peanut shell-based carbons investigated by Kermit Wilson *et al*., 2005, Mu. Naushad *et al.*. 2008, Anna Witek-Krowiak *et al*. 2010 and Seyda Tasar *et al*., 2014 using difreent treatment methods. Lead; Pb(II) ions removal from aqueous solutions using peanut shell as adsorbent has also been done. The raw peanut shell was converted into an efficient adsorbent without any treatment. The biosorption of $Pb^{2+}$ ions onto peanut shells from an aqueous solution was studied in a batch system as a function of temperature, pH of the solution, contact time, initial concentration of $Pb^{2+}$ ions, and dose of adseorbent. The linear forms of the isotherms and kinetic models were used to determine the biosorption mechanism. The removal of $Pb^{2+}$ ( q max ) reached approximately 39 mg/mg using Langmuir at higher concentration at an optimum pH of 5.5, using 2g/L of adsorbent in 2h of equilibration time(Taşar, Kaya, & Özer, 2014). All results showed that peanut shells biomass is an attractive, alternative low-cost biosorbent for removal of heavy metal ions from aqueous media (Ali & Naushad, 2012; Taşar *et al.*,, 2014; Wilson *et al*., 2006; Witek-Krowiak *et al.*, 2011).

### 2.6 Application Of Adsorption

Adsorption plays a major role in the environmental pollution control and life supporting systems. This technique also was found to be highly efficient and feasible for the removal of color in terms of initial cost, simplicity of design, ease of operation and in sensivity to toxic substances (Ezechi *et al*, 2015; Sabrin A, 2015).

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. However, amongst all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater. Because of their great capacity to adsorb dyes, activated carbon are the most effective adsorbents. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties (Kharub, 2012).

There are many advantages of adsorption process such as: less land area required, lower sensitivity to diurnal variation, greater flexibility in the design and operation, superior removal of organic contaminants, high dye removal efficiency, most of time dose not form harmful substances, and easy of operation (Sun *et al.,* 2013).

Nowadays, activated carbon finds wide application in many areas, but especially in the environmental field reated with treatment and purification. Aside from environmental pollution control, activated carbon is mainly used in industry in various liquid and gas phase adsorptions (Aktaş & Ferhan, 2012). Activated carbon has many applications including water treatment, chemical and petroleum industries, separation, purification, catalysis, energy storage, batteries, fuel cells, nuclear power stations, electrodes for electric double layer capacitors, pharmaceutical, hydrometallurgy and others like used for decolourization, deodorization and taste removal purposes and intended for color removal in liquid phase system in food industries, used for harmful chemical and drug adsorption purpose in medicine, In gas cleaning applications, activated carbon is used for air filters and air conditioning purpose, and used for gold recovery from leached liquors in mineral industries (Adib *et al*., 2015) and used for product purification in suger refining , for purification of chemicals and enzymes in deffrent industries and purification in the clothing, textile, personal care, cosmetics, and pharmaceutical industries(Aktaş & Ferhan, 2012).

## 2.7 Adsorption Isotherm and Kinetics Models

### 2.7.1 Adsorption Isotherm Models

An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. The adsorption isotherm is the primary source of information on the adsorption process (Aktaş & Ferhan, 2012). Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems and provides information on the capacity of the adsorbent (Banerjee & Sharma, 2013).

An adsorption isotherm describes the relationship between the amount of adsorbate up taken by the adsorbent and the adsorbate concentration remained in the solution (Ghaedi *et al.*, 2012). If the adsorbent and adsorbate are contacted long enough, equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by adsorption isotherms. For practical purposes, it can be used to select the appropriate activated carbon type, to estimate the carbon service life, and to test the remaining adsorption capacity of a carbon adsorber in continuous-flow operation. In order to investigate the adsorption isotherm, there are two the most widely used mathematical expressions of adsorption equilibrium isotherms have been analyzed: Langmuir and Freundlich isotherm model (Banerjee & Sharma, 2013; Ghaedi *et al.*, 2012).

#### 2.7.1.1 Freundlich isotherm model

The Freundlich isotherm can be used to determine the adsorption capacity of activated carbon over a wide range of concentrations. Adsorbents that follow the Freundlich isotherm equation are assumed to have a heterogeneous surface consisting of sites with different adsorption potentials, and each site is assumed to adsorb molecules (Aktaş & Ferhan, 2012). Freundlich equation suggests multilayer adsorption and the sorption energy exponentially decreased on completion of the sorption centers of an adsorbent. The Freundlich equation as shown below is very widely used for activated carbon applications (Sun *et al.*, 2013, Aktaş & Ferhan, 2012).

$$q = KfCe^{1/n} \quad (2.1)$$

Where: q= Adsorption capacity (mg adsorbate adsorbed per g adsorbent)

Ce= Equilibrium adsorbate concentration, ($Ms/L^3$)

$k_f$= Freundlich exponent; an indicator of adsorption capacity

1/n= Freundlich slope; adsorption intensity

The linearized form of Freundlich model is expressed as follows:

$$\log(qe) = \log(kf) + \frac{1}{n}\log(Ce) \quad (2.2)$$

Where: qe = Amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g)

Ce = Equilibrium concentration of adsorbate (mg/L)

$k_f$ = Freundlich isotherm constant (mg/g); indicate the adsorption capacity

1/ n = Adsorption intensity or heterogeneity factor, used to verify types of adsorption

1/**n** indicates the degree of non-linearity between solution concentration and adsorption. If the value of 1/n is equal to unity(1), the adsorption is linear; if the value is below unity, this implies that adsorption process is chemical; if the value is above unity, adsorption is a favorable physical process (Srinivasan *et al.*, 2013).

### 2.7.1.2 Langmuir isotherm model

Langmuir adsorption isotherm is one of the most popular isotherms for the removal of dyes, heavy metals, organic pollutant by adsorption onto activated carbon, clay, agricultural waste, industrial waste, e.t.c (Banerjee & Sharma, 2013). It is based on the assumption that the adsorption process takes place at specific homogeneous sites within the adsorbent surface and that once a dye molecule occupies a site, no further adsorption can take place at that site, which concluded that the process is monolayer in nature (Ghaedi *et al.*, 2012). The area of site is fixed, quantity determined only by the geometry of the surface, and the adsorption energy is the same at all sites. In addition, the adsorbed molecules cannot migrate across the surface or interact with neighboring molecules. The Langmuir isotherm model estimates the maximum adsorption capacity produced from the complete monolayer coverage on the adsorbent surface. Based upon the above assumptions, Langmuir represented by equation (Aktaş & Ferhan, 2012; Banerjee & Sharma, 2013)

$$qe = \frac{qmKLCe}{1+KLCe} \quad (2.3)$$

Langmuir parameters were determined by transforming the above equation into linear form:

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{qmKLCe} \quad (2.4)$$

Where: qe = amount of adsorbed per gram of the adsorbent at equilibrium (mg/g).

qm = maximum monolayer coverage capacity (mg/g)

Ce = equilibrium concentration of adsorbate (mg/L)

$k_L$ = Langmuir isotherm constant (L/mg)

The values $q_m$ (maximum adsorption capacity) and $k_L$ were computed from the intercept (1/qm) and slope ($1/q_m k_L$) of the Langmuir plot of 1/qe versus 1/Ce or the plot between Ce/qe versus Ce.

To determine whether the profile of the isotherm is favourable or unfavourable, it is necessary to consider the dimensionless factor $R_L$, given by the following Langmuir equation in terms of a dimensionless separation factor $R_L$, which is a dimensionless constant, referred to as separation factor or equilibrium parameter (Banerjee & Sharma, 2013)

$$RL = \frac{1}{1+KLCo} \quad (2.5)$$

Where: $R_L$= Langmuir equilibrium parameter and Co= the initial concentration (mg/l)

The value of $R_L$ indicates the shape of the isotherm to be either unfavorable ($R_L$>1), linear ($R_L$=1), favorable (0 < $R_L$ < 1) or irreversible ($R_L$ = 0). By using the dimensionless separation factor $R_L$ from the Langmuir equation, adsorption isotherms can be successfully used to have an idea on the reversibility of adsorption.

### 2.7.2 Adsorption Kinetics

The dynamics of the adsorption can be studied by the kinetics of adsorption in terms of the order of the rate constant. The adsorption rate is an important factor for a better choice of material to be used as an adsorbent; where the adsorbent should have a large adsorption capacity and a fast adsorption rate. Adsorption kinetics models are used to explain the adsorption mechanism and

adsorption characteristic (Aljeboree *et al.*, 2014). In other to investigate the mechanism of the process and the potential rate controlling steps, such as mass transport, pore diffusion and chemical reaction processes; kinetic models have been used to fit experimental data (Joseph *et al.*, 2016). The results of these kinetic models are useful for the design and optimization of effluent treatment process in bulk at industrial level (Srinivasan *et al.*, 2013). Most of the time the experimental data analyzed using pseudo-1$^{st}$ and 2$^{nd}$ order models, and kinetic constants were calculated for concentration (M. S¸aban Tanyildizi, 2011)

### 2.7.2.1 Pseudo first order kinetics model

Pseudo first-order kinetics model is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase. A linear form of the pseudo first order kinetic model known as Lagergren rate equation expressed as follows (Aktaş & Ferhan, 2012):

$$\log\ (qe - qt) = \log(qe)\ \ - (\frac{k1t}{2.303}) \qquad (2.6)$$

Where: qe and qt (mg/g) = Adsorption capacity at equilibrium and at time t, respectively

$k_1$ ($min^{-1}$) = Rate constant of pseudo first-order kinetics

The plot of log (qe – qt) versus t should give a linear relationship from which $k_1$ and qe can be determined from the slop and intercept of the plot, respectively.

### 2.7.2.2 Pseudo second-order kinetics model

The adsorption kinetics was also described as pseudo-second order kinetics using equation;

$$\frac{t}{qt} = \frac{1}{k2qe2} + \left(\frac{1}{qe}\right)t \qquad (2.7)$$

Where: qe and qt = adsorption capacities at equilibrium and at time t, respectively (mg/g)

$k_2$ = rate constant of pseudo-second-order sorption (g/mg/min)

If Pseudo-second order kinetics is applicable, the plot of t/qt against t should give a linear relationship, from which qe and $k_2$ can be determined from the slope and intercept of the plot (Ghaedi *et al.*, 2012).

# 3. METHODOLOGY

## 3.1 Material and Equipment

The major equipment's used are Tubular Furnace with a stainless steel tubular reactor (Carbolite), UV-Vis spectrophotometer (Spector UV-VIS double beam PC; UVD-3200), furnace (Box-type Resistance Furnace, Model SX-2f.12), centrifuge (Universal 320 R), Shaker (Excella E24R), vacuum filters, pH meter, digital balance, oven and sieving equipment found in SCBD, AAiT. The laboratory wares are volumetric flask, teflon sheets, vacuum desiccators, beaker, conical flask, micropipettes, burette, mortar & pestle. All chemicals used in this study are analytical grade includes; hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium nitrate ($KNO_{3)}$, nitrogen gas($N_2$) which is 99.6% pure was used as an inert, Golden Yellow 28 dye powder form see figure 3.1(a) and peanut shell as adsorbate see figure 3.1(b) . Distilled water was used for all solution and dilution.

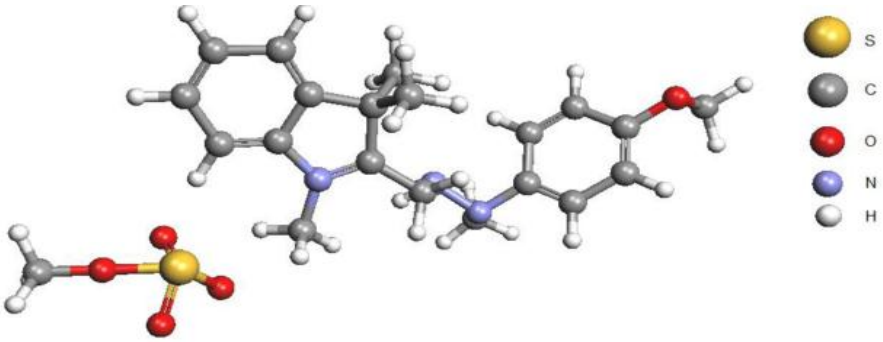
**(a)**

**(b)**

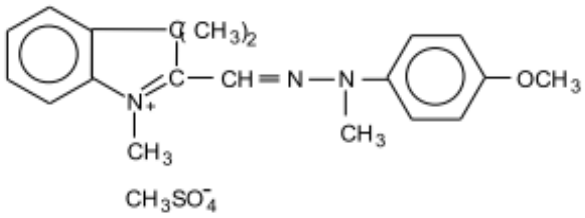
Figure 3.1 (a) Sample of GY 28 dye powder form and (b) Sample of peanut shell

### 3.2 Adsorbate

Cationic (Basic) dye; Golden yellow dye called Acrylic Yellow 28 Azo Dye type, highly transparent clean, orange powder, with water soluble dye property and the sun fastness is Excellent; obtained from KK textile industry P.L.C, Akaki Kaliti: Southern Addis Abeba, Ethiopia; as a gift was chosen as the adsorbate in this study, and not purified prior to use. The stock solution was prepared by dissolving 1.0 g of GY 28 dye in one liter (1L) distilled water. The chemical formula of Golden Yellow dye $C_{21}H_{27}N_3O_5S$, its molecular weight is 433.52 g/mol, its molecular structure see figure 3.2(a) and its structural formula see figure 3.2 (b).




**(a)**




**(b)**

Figure 3.2 (a) 3D molecular structure of GY 28 dye (Adil Jaafar and A. Boussaoud ,2014) and (b) Structure formula of GY 28 dye (Filipkowska *et al.*,2015)

### 3.3 Collecting, Pretreatment and Characterizing Of Peanut Shell

The raw material used in this study, peanut shell, for production of activated carbon was collected from local industry Hamaressa Edible Oil Sh.Co, located around Hamaressa in Oromiya Regional State, Hararge Eastern Ethiopia. It was washed thoroughly with distilled water to remove any dust & impurities and then oven dried at 105°C for 24 hours for removal of moisture. The

peanut shell were crushed or ground by milling machines (ACHTUNG , Germany), and sieved to a particle size between the range of 1.0–2.0mm (10 to 18 mesh) in diameter using standard sieves in laboratory and then stored in air tight plastic in desiccators denoted as PS for further experiment.

### 3.3.1 Proximate and ultimate analysis of peanut shell

The proximate analysis of PS is a means of determining the distribution of products obtained when the sample is heated under specified conditions. Proximate analysis (volatile matter (ASTM D 3175), ash content (ASTM D 3174), moisture content (ASTM D 3173), and fixed carbon (ASTM D 3172) of the peanut shell were measured using the method of ASTM (ASTM, 2004). Proximate analysis is the most often used analysis for characterizing a material in connection with their utilization.

**Determination of moisture content**

The moisture content of the sample was determined by weighing 1.0g of sample into a pre-weighed crucible and drying it in an oven at a temperature of 105 ± 5°C till the constant weight dry matter was obtained. The percentage moisture content was computed as follows:

$$Moisture\ content(\%) = (\frac{W1-W2}{W1})*100 \quad (3.1)$$

Where: $w_1$= Weight of crucible and sample before drying (g)

$w_2$= Weight of crucible and sample after drying (g)

**Determination of ash content**

Ash is an inorganic residue remaining after the material has been completely burnt at a temperature of 650 °C in furnace. It is the aggregate of all non-volatile inorganic elements. About 1.0 g of dried sample was weighed into a crucible ($w_1$) and incinerated at 650°C for 3 hrs in furnace. The crucible was cooled in desiccators and reweighed ($w_2$). The % ash content of the sample was calculated as follows:

$$Ash\ content(\%) = (\frac{W1-W2}{W1})*100 \quad (3.2)$$

Where: $w_1$ and $w_2$ = Weight of crucible and sample before and after incineration(g) respectively

**Determination of volatile matter content**

About 1.0g of dried sample was weighed into a crucible ($w_1$) and incinerated at 950°C for 7 minute in furnace. This procedure is undertaken without contact with air under standardized conditions. The crucible was then cooled in desiccators and reweighed ($w_2$). The % volatile of the sample was calculated as follows:

$$Volatile\ matter\ (\%) = (\frac{W1-W2}{W1})*100 \quad (3.3)$$

Where: $w_1$= Weight of crucible and sample before incineration (g)

$w_2$= Weight of crucible and sample after incineration (g)

**Determination of fixed carbon content**

Fixed carbon is a calculated value and it is the resultant of summation of percentage moisture, ash, and volatile matter content subtracted from 100. All percentages shall be on the same moisture reference base. The % fixed carbon of the sample was calculated as follow:

$$Fixed\ carbon\ (\%) = 100 - [moisture\ (\%) + ash\ (\%) + volatile\ matter\ (\%)] \quad (3.4)$$

**3.4 Preparation and Characterization of the Modified Adsorbent**

Two samples of activated carbon were prepared in this study and the preparation methodologies were described as follows;

**Conventional pyrolysis**; For the preparation of activated carbon by conventional pyrolysis means that the pretreated PS was subjected to direct carbonization without applying any type of activating agent to produce simple charcoal called Bio-char. 50gm of the PS precursor (particle size between 1.0 - 2.0 mm) were inserted in a stainless steel tubular reactor which was equipped with a tubular furnace, nitrogen gas inlet and control unit (temperature and heating rate).

**Pyrolysis followed by chemical activation**; For the activated carbon modifications, 50g of the pretreated PS was first soaked in fixed amounts of activating chemicals (50gm of NaOH ) with 250 ml aqueous solution in 1000ml beaker. The IR denoted by the ratio of NaOH weight to PS weight was maintained at 1:1 (wt/wt) and the mixture of the pretreated raw material (PS) and activating agent was well mixed and stirred for 24 hr at room temperature. After a day, PS precur-

sor was separated from the mixture by mechanical filtration with a sieve if the solution more excess than it was placed in an electrical oven dried at 110°C for 24 hr to remove the remaining moisture. Once again, after a day the 50gm of impregnated sample was placed in a horizontal stainless steel tubular reactor equipped with horizontal tubular furnace, nitrogen gas inlet and control unit.

In both case; the PS precursor and impregnated samples were heated to the final carbonizations temperature under a continuous nitrogen flow (10bar) with a constant heating rate ($10^{o}$C/min) and activation time (2:30 hr) by an activation temperatures of 400, 500 and 600$^{o}$C for each sample. After carbonizations, the carbonized materials were cooled down under room T$^{o}$ and washed frequently several times with 0.1 M HCl and hot distilled water (at 60-70$^{o}$C) until the pH of the washing solution reached 7. Finally, the samples were dried in an oven at a temperature of 110 $^{o}$C for overnight and then grounded & sieved. The particle size distribution of the activated carbon obtained in this manner was determined to be between 250-600 µm or (0.25–0.6 mm). The activated carbons were stored in air tight glass bottle in desiccators until it is needed by denoted Bi-Ch and BM respectively.

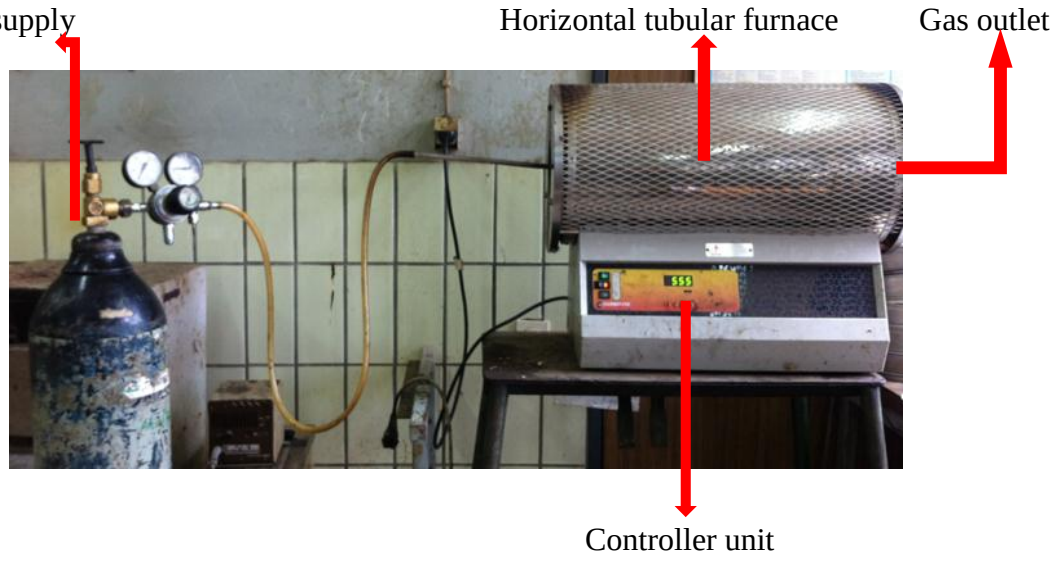



Figure 3.3 The carbonization equipment setup for activated carbon production

### 3.4.1 Effect of Carbonization Temperature

Temperature, particularly the final activation temperature, affects the characteristic of the activated carbon produced. Recently, as reported by several authors, activation temperature significantly affects the production yield of activated carbon and also the surface area of activated carbon (Adib *et al.,* 2015; Ahmad & Hameed, 2010). The temperature used as low as 200°C and up high to 1100 °C. The optimum temperatures have been reported to be between 400°C to 600°C by most of earlier researchers irrespective of the time of activation and impregnation ratio for different lignocellulosic raw materials (Srinivasakannan *et al.*, 2004). The activation temperature can affect the yield of the activated carbon continuously. The yield of activated carbon (Y) can be calculated by the equation 3.5.

$$Y\% = \frac{Wf}{Wo} * 100 \qquad (3.5)$$

Where: $w_f$ = the dry weight of final activated; (g)

$w_o$= the dry weight of precursor; (g)

## 3.5 Characteristics of Prepared Adsorbent

### 3.5.1 BET specific surface area analysis

The BET specific surface area, pore volume distribution, micropore surface area were determined by using a surface area analyzer, Quantachrome Instruments ©2000-11 version 5.04, which is based on the principle of multilayer adsorption of $N_2$ as a function of relative pressure. Before analyzing the sample in BET, it was kept for degassing at 573K for 3hr to detach any gaseous impurities within the sample. Surface area is one of the important parameters in deciding the quality and efficiency of activated carbons.

### 3.5.2 Point of zero charge determination

The pH value at which the surface charge is zero is called the point of zero charge (PZC). The point of zero charge (PZC) for PS and BM5 was investigated by the solid addition method (Ezechi *et al.,* 2015). 500ml of $KNO_3$ (0.1N) in the PH range of 2 to 10 was prepared in 9 different flasks. 45ml of $KNO_3$ was taken from the 500ml and initial pH of solution were adjusted by adding drops of 0.1N NaOH and 0.1N HCl solutions and 0.5 g of PS and BM5 samples are add-

ed to each flasks and shake for 48hrs at room temperature. Finally, the pH was measured and recorded. The total charge adsorbed (ΔpH) on PS and BM5 surface was determined by the difference between pH after and pH before 48 hrs. The pH values (pH of 1 to 10) are plotted along the x-axis and ΔpH along y-axis, the data obtained from the experiment are plotted and the intersection point is taken as a reference for deciding the $pH_{PZC}$ value.

### 3.5.3 XRD analysis

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. X-ray diffraction yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system. The structure of activated carbon was determined by X-ray diffraction method using Bruker D8 Advance X with CuKα radiation, 2θ scan angle varies from 10-70º, scan time is 1 s step, scanning angle of 0.03º.

### 3.5.4 Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. Details of functional group presents on the surface of the material were obtained from FTIR studies. The FTIR analyses were conducted using Spectrum 65 FT-IR (PerkinElmer) in the wave range 4000 - 400 $cm^{-1}$ using KBr pellets see figure 3.4. The raw material: PS, prepared activated carbon and dye loaded activated carbon samples for the analysis were first milled in a ceramic pestle and mortal to powdery conditions. The powder was then mixed with KBr particles to make it suitable to infrared analysis. The mixture was then pressed to a small thickness, slightly below 1mm, required for FTIR analysis.

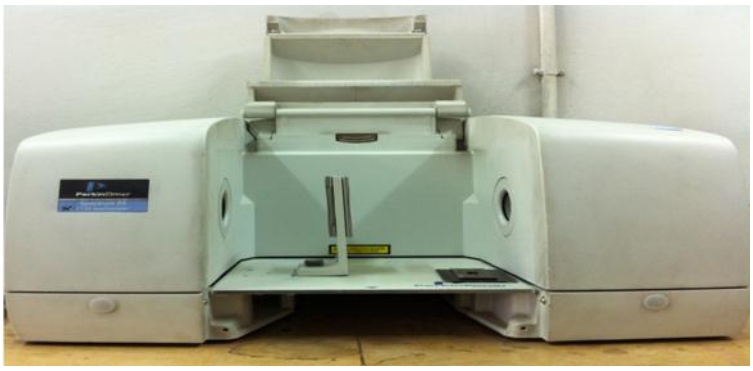


Figure 3.4 FTIR Spectrometer (PerkinElmer Spectrum 65 FT-IR)

### 3.6 Dye Adsorption Studies

Batch dye adsorption experiments were performed in order to determine the optimum adsorption capacity of adsorbent, to generate adsorption equilibrium and adsorption kinetics data. These studies were conducted in a set of 250 ml Erlenmeyer flasks containing 0.5 g adsorbent (Bi-Ch & BM) dose of particle size between 0.25–0.60mm and 100ml dye solutions with various initial dye concentrations, pH of the solution and adsorption contact time. The flasks were agitated in isothermal shaker at 150 rpm and 30 $^{O}$C and also the pH of the solution was adjusted by using 0.1M NaOH and 0.1M HCl to bring to the required pH. The effect of initial concentrations of GY 28 dye (10, 50, 100, 150 ppm), time (10, 30, 60 and 90) and pH of the solution (1.5, 3.5, 6.5 and 10) on the adsorptive removal of GY 28 from an aqueous solution were investigated. First, 1000 ppm GY 28 stock solution was prepared by dissolving 1 g powdered GY 28 in 1000ml distilled water. Taking some different concentration of GY 28 from the stock solution and diluting it by 100ml distilled water in 250ml Erlenmeyer flasks, a standard calibration curve is prepared. The sample withdraw were centrifuged for 5 min and 6000 rpm to clarify the adsorbent from the supernatant. The dye concentration before and after adsorption were determined using UV-Vis spectrophotometer (Spector UV-VIS double beam PC; UVD-3200) at wavelength 438 nm.

The adsorption experiment was performed by varying several parameters like pH, initial dye concentration, and contact time at constant temperature.

*pH*:- one of the pivotal factors influencing not only the surface charge (ionization/dissociation) of the adsorbent, but also the solution dye chemistry. The effects of initial pH on GY 28 solution

using BM were evaluated within a range between 2 and 10. The pH of the test solutions were adjusted by using HCl and NaOH with a digital pH meter.

*Concentration:* - The effect of concentration on adsorption of GY 28 by a BM was investigated keeping other experimental parameters (pH, particle size, adsorbent dosage and temperature) constant. After undergoing meticulous experimental procedures, a desired concentration range of 10 to 150 ppm was selected and fixed amount of adsorbent (0.5 g) was added to these solutions.

*Contact time*: - This study aided in acquiring the optimum time duration for adsorption during the experiment. Fixed amount of adsorbent was taken in single concentration solution for duration of about 360 min and shaken at a speed of 150 rpm at constant temperatures i.e., 25$\pm$5 $^{O}$C. The supernatant solution was observed after every 30 min.

The absorbance data obtained from the UV-Vis spectroscopy is recorded and inserted into the initially prepared standard calibration curve and the concentration of GY 28 dye in terms of ppm is obtained from the curve. The adsorption performances of the prepared activated carbons were calculated using equation below. All experiments were performed in duplicates. GY 28 uptake at at equilibrium, $q_e$ ($mgg^{-1}$), was calculated by the following equation:

$$qe = \frac{(Ci - Ce)}{m} * V \tag{3.6}$$

Where: $C_i$, and $C_e$ are the initial, and equilibrium concentration at time of dye respectively.

v = volume of the solution (mL) and m = mass of adsorbent used (gm)

The percentage removal of GY 28 dye removal percentage was calculated as follow:

$$\%R = \frac{(Ci - C)}{Ci} * 100 \tag{3.7}$$

Where: C = Remaining concentration of GY 28 dye after adsorption (ppm)

### 3.7 Data analysis using Design Expert software

Experimental design technique is a very useful tool adsorption study as it provides statistical models which help in understanding the interactions among the parameters that have been optimized. Data analysis also was performed by Design Expert 6.0.8 software using full factorial design. The experiment was designed to investigate the single and interaction effects of selected

operating conditions (initial dye concentration, pH, and contact time) on adsorption capacity and removal efficiency of the BM5. The analysis resulted in 27 experiments of the data. The factors and levels are illustrated in Table 3.1. The pH level points were selected in the table we will try to see the effect of adsorption processes in concentrated zone.

Table 3.1 Factors and levels of adsorption studying parameters

| Parameters | Unit | Level | | |
|---|---|---|---|---|
| pH | - | 3 | 6.5 | 10 |
| Contact time | min | 30 | 60 | 90 |
| Initial concentration | ppm | 50 | 100 | 150 |

### 3.8 Adsorption Isotherms and Kinetics models

The amount of dye adsorbed in a state of equilibrium is one of the key parameters in the study of adsorption processes. This information is usually presented as adsorption isotherms, representing the relation between the amount of dye adsorbed on the surface of the adsorbent (qe) and the equilibrium concentration in the liquid phase (Ce). The quantity of adsorbed molecules per mass of adsorbent is a function of the concentration at a constant temperature and characteristics of the fluid and solid phases in our case. To determine the influence of these parameters, different mathematical models have been proposed in the literature, the Langmuir and Freundlich models being among the most commonly.

The kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from the aqueous solution at different time intervals. In order to understand the process of adsorption, the two most common kinetic models were applied to analyze the experimental data; the linear form of pseudo first and pseudo second order kinetics model. In this study, the two models were tested for GY 28 dye on the BM5 AC. The best fit model was determined depending on the linear correlation coefficient $R^2$.

Batch adsorption studies were conducted in a set of 300 ml Erlenmeyer flasks containing 0.5gm adsorbent dose and 200 ml dye solutions with 50 and 150 ppm initial GY 28 dye concentrations at pH of 10. The flasks were agitated in isothermal shaker at 150 rpm at 30 and 40 $^{o}$C. The samples were taken at different time interval until the equilibrium was reached. The experimental data were analyzed for equilibrium isotherm and kinetic studies.

# 4. RESULT AND DISCUSSIONS

## 4.1 Characterizations of raw peanut shell composition

The characterization results of PS are shown in Table 4.1 and 4.2. The proximate and ultimate analysis of PS was done by standard ASTM 2004 procedures.

Table 4.1 Proximate Analysis; @ Wet basis and ASTM 2004 method

| Parameters | Method | Weight wt% |
|---|---|---|
| Moisture content | ASTM D 31 73 | 2.02 |
| Ash content | ASTM D 31 74 | 1.81 |
| Volatile matter | ASTM D 31 75 | 78.1 |
| Fixed carbon | From difference | 18.07 |
| pH* | ASTM D 38 38 | 5.13 |
| Point of zero charge* | Solid addition | 6.56 |

*** Unit less ; using direct measurement**

The proximate analyses of the samples were carried out see Table 4.1 and observed that the pH value of the samples is 5.13 for PS, indicating slightly acidic to neutral samples. It can be observed that the concentration of the total acidic sites was greater than the concentration of the basic sites for PS; so, the surfaces of these adsorbents were acidic. And the fixed carbons have 18.07% due to high value of volatile matter content and the lower ash content ware found in the raw material; this indicated that the PS can have a good carbon content used for activated carbon.

The elemental analyzer was used to the rapid determination of carbon, hydrogen, nitrogen and sulfur (CHNS) contents in organic matrices and other types of materials. In its simplest form, simultaneous CHNS analysis requires high temperature combustion in an oxygen-rich environment. This combustion can be carried out under both static conditions i.e. introduction of a set volume of oxygen conditions i.e. a constant flow of oxygen for a set period of time. Often, catalysts are also added to the combustion tube in order to aid conversion. In the combustion process (furnace at 1000 $^{o}$C), carbon is converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/ oxides of nitrogen and sulfur to sulfur dioxide. The ultimate analysis for raw materials PS; also observed in this study show in Table 4.2.

Table 4.2 Results of elemental analysis; @ dry basis

| Elemental content | Method | wt% |
|---|---|---|
| Carbon | Elemental analyzer | 52.73 |
| Sulfur | Elemental analyzer | 0.12 |
| Hydrogen | Elemental analyzer | 6.10 |
| Nitrogen | Elemental analyzer | 1.33 |
| *Oxygen | From difference | 39.83 |

***Calculated by difference;**

According to the Table 4.2, the highest amounts corresponded to the Carbone and the Oxygen which prove the organic nature of the adsorbent.

### 4.2 Yield of prepared activated carbon

Carbonization temperature plays an important role on the yield of modified activated carbon. From the Table 4.3 below show the pyrolysis phenomenon of raw PS (particle size 0.25–0.60 mm) and impregnated one under inert nitrogen. The characteristics of the activated carbon vary with impregnation ratio, activation temperature and composition of the gas used for heating. For this study we were used different carbonization temperatures (400, 500, 600$^{o}$C) at a constant impregnation ratio (1:1 by wt), activation time (2:30hr) and heating rates (10$^{o}$C/min). In this way, six different adsorbent samples were prepared and their performance towards GY 28 dye removal was investigated.

Table 4.3 (a) and (b) below shows the effect of carbonization temperature to the yield of Bi-Ch and BM activated carbon, which decreased progressively with increasing temperature from 400 to 600 $^{o}$C at the fixed holding time of 2:30 hr. Any nutshell commonly consists of cellulose, hemi-cellulose and lignin. The decomposition of two major components (equivalent to approximately 70% of the overall mass) in raw PS, namely, hemicellulose 14.7 % and cellulose 40.5%, occurred in the temperature range between 250–430 $^{o}$C and lignin 26.4%, proceeded slowly with temperature between 230–550$^{o}$C (Malik, Ramteke, & Wate, 2006). For a temperature of 555 $^{o}$C, most of these two components had been converted to gaseous products such as $H_2O$, CO,$CO_2$ and $CH_4$ or stabilized char but the decomposition of another major component, lignin, proceeded slowly with temperature in which the yield decreased. The yield percentage for variation in carbonization temperature is good agreement with the above statement up to 555$^{o}$C, maximum vola-

tile matter is released due to decomposition of cellulose, hemi-cellulose and lignin, that's why yield percentage remains almost constant on increase of temperature because there is no volatile matter left for release (Chen *et al.*, 2015;Yang, 2007). The hot discharge gases (smoke) and the volatile matter passing out from the carbonized reactor is direct released to the atmosphere through a rubber tubes.

Form laboratory analysis the carbonization yield was determined as follows:

$$Y(\%) = \left( weight\ of\ carbon\ produced \Big/ weight\ of\ raw\ sample\ used \right) * 100 \qquad (4.1)$$

From the equation 4.1; the percentage yield of the modified carbon at different carbonization temperatures presented in Table 4.3 a and b.

Table 4.3 (a) Effect of carbonization temperatures on yield of Bio-char activated carbon

| Mass of biomass, gm | Carbonization T$^{o}$, $^{o}$C | Mass of Bio-char, gm | Yield, % |
|---|---|---|---|
| 50 | 400 | 17.5 | 34.9 |
| 50 | 500 | 16.2 | 32.4 |
| 50 | 600 | 15.3 | 30.6 |
| 100 | 500 | 33.6 | 33.6 |

**@ Activation time 2:30 hr and heating rate 10 $^{o}$C/min**

Table 4.3 b) Effect of carbonization temperatures on yield of BM activated carbon

| Mass of biomass, gm | Carbonization T$^{o}$, $^{o}$C | Mass of BM, gm | Yield, % |
|---|---|---|---|
| 50 | 400 | 27.2 | 54.4 |
| 50 | 500 | 24.5 | 49.0 |
| 50 | 600 | 21.2 | 42.4 |
| 100 | 500 | 55.7 | 55.7 |

**@ Activation time 2:30 hr and heating rate 10 oC/min**

From Table 4.3a we observed that all the samples had a low percentage yield after carbonization having recorded their yield below 35%. But after chemical activation, the percentage yield was very high in all the samples at all temperatures used. Moreover, the yield of carbon in chemical activation is usually higher than those in physical activation because the chemical agents used

are substances with dehydrogenation properties that inhibit formation of tar and reduce the production of other volatile products (M, P, & Ram, 2012)

It could also observe that the percentage yield at a higher temperature is lower than at lower temperature even when carbonized at a longer period. This is because increase in temperature resulted in more volatile components of the precursor materials being lost, and hence a decreasing percentage yield. As seen in the figure 4.1, the carbonization temperature has significant effect, at 400$^{o}$C for PS carbonized at 2:30 hr, the Bi-char yield was 34.9% but decreased to 30.6% at 600$^{o}$C. Similar trends have been observed for impregnated as well; the yield of 54.4% was obtained at 400$^{o}$C and decreased to 42.4% at 600$^{o}$C.

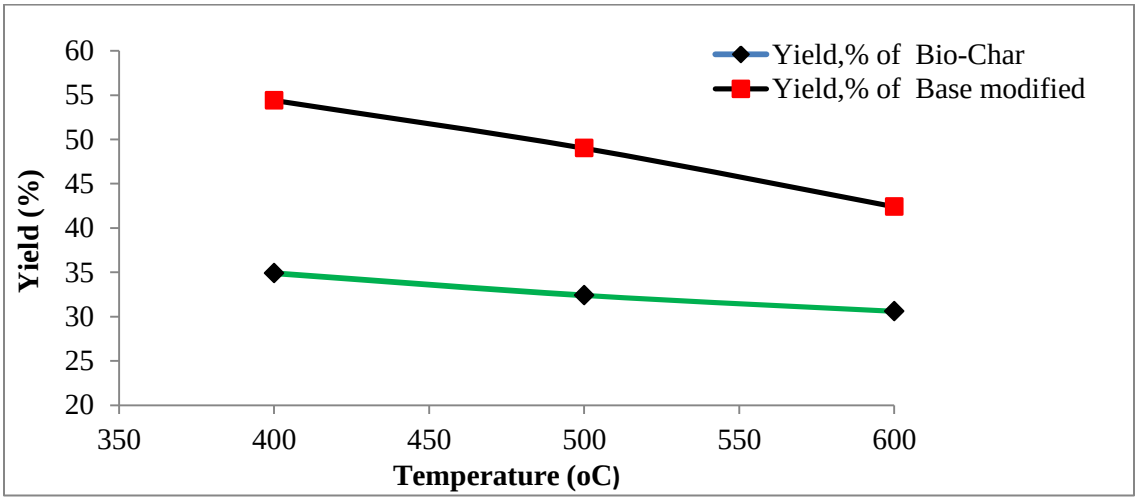



Figure 4.1 Effect of carbonization temperatures on yield of prepared AC

As shown in the figure above, the final yield is strongly dependent on the operating conditions during preparation of AC. As the temperature of carbonization increases, the prepared activated carbon % yield decreases.

### 4.3 Surface Characterization of the prepared Adsorbent

#### 4.3.1 Brunauer-Emmett-Teller; BET Method ($N_2$ adsorption isotherms)

Specific surface area, total pore volume, and pore radius are significant indicators for any solid adsorbent. Application of an activation step before pyrolysis would increase the BET surface areas of these chars (Apaydın-varol & Pütün, 2012). The surface physical parameters obtained from the $N_2$ adsorption isotherms for all samples are shown in Table 4.4. The physical properties

of the base modified sample; BM were improved when compared to other two samples; PS and Bi-Ch. Chemical activation than follow pyrolysis is advantageous because is easy and fast, resulting in a material with high porosity. Thus the activation processes applied on the PS, significantly changed their physical properties, resulting in materials with high surface area and porosity. As shown in Table 4.4, among prepared activated carbons, modified activated carbon, BM5 @500$^{o}$C (973m$^{2}$/g) showed better activity than conventional pyrolysis activated carbon, BiCh5 @500$^{o}$C (168.7m$^{2}$/g) and also the other type of prepared activated carbons. The difference in the adsorption efficiency of these prepared carbons proved on the properties of activated carbon for dye treatment.

Table 4.4 Surface physical characteristics of prepared activated carbon

| AC | Carbonization T $^{o}$C | BET surface area ($m^2g^{-1}$) | Ash (%) | Pretreatment of dye solution |
|---|---|---|---|---|
| RPS | - | 2 | 1.81 | 20.8 |
| Bi-Ch4 | 400 | 146.6 | 2.6 | 32.3 |
| Bi-Ch5 | 500 | 168.7 | 3.2 | 38.6 |
| Bi-Ch6 | 600 | 176.9 | 4.4 | 41.8 |
| BM4 | 400 | 540.3 | 5.6 | 59.6 |
| BM5 | 500 | 973.6 | 7.8 | 76.7 |
| BM6 | 600 | 1012.8 | 11.6 | 77.6 |

Generally, the larger the specific surface area of the adsorbent, the better its adsorption performance while the larger the ash content of the adsorbent, it will be decreased the adsorption efficiency. So based on the BET surface area, ash content and pre-treatment percentage removal of BM5 prepared activated carbon had better value of adsorption efficiency by considering the energy consumptions used for the BM6 activated carbon preparation. Therefore based on Table 4.4 BM5 activated carbon was preferred for the potential of adsorption efficiency from aqueous dye solution. Based on Honoré *et al*., 2014 studied the ash content is a characteristic of carbon values basically greater than 20 % indicate insufficient carbonization. This means that activated carbon little by little has lower efficiency of adsorption.

### 4.3.2 Proximate analysis of BM5 AC

The result of the proximate analysis done on the BM5 is presented in Table 4.5. Moisture content, ash content, volatile matter, fixed carbon and density ware determined using ASTM 2004.

Table 4.5 proximate analysis of BM5 activated carbon @ dry basis

| Parameters | Method | Weight wt% |
|---|---|---|
| Moisture content | ASTM D 2867 | 9.96 |
| Ash content | ASTM D 2866 | 7.8 |
| Volatile matter | ASTM D 3175 | 36.24 |
| Fixed carbon | From difference | 46.0 |

The ash content and percentage fixed carbon compare favourable with those for the commercial activated carbon. Therefore, from different literature studies prepared activated carbon sample with higher percentage fixed carbon are expected to have high adsorption capacities.

### 4.3.3 Point of zero charge analysis

The adsorption of the charged dye group onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which is in turn influenced by the solution pH. The point of zero charge ($pH_{PZC}$) is the pH at which the surface exhibits net zero charge. $pH_{PZC}$ was determined by batch equilibration method in which nine different solutions were prepared having pH values ranging from 2–10. A portion of the sample (0.5 gm) was then added to each flask, the flasks were shaken for 48 hr at 150 rpm, and the final pH was then measured. The pHpzc is the point where the curve of $\Delta pH$ vs $pH_i$ intersects the line $pH_i = pH_f$. The significance of pHpzc of activated carbon surface is that at pH values below $pH_{PZC}$, the activated carbon had a net positive charge, since the electrostatic attraction between positively charged adsorption sites and positively charged dye causes a decrease in the dye removal. On the other hand, if the solution pH has greater than that of pHpzc of activated carbons, the surface of the carbons will bear negatively charged and cations may be adsorbed on the surface (Seey *et al.*, 2012). The pHpzc of PS was found to be 6.56 see Table 4.1 but for prepared activated carbon BM5 was found to be 7.8. The $pH_{PZC}$ value for BM5 activated carbon is shown in the figure 4.2 below.

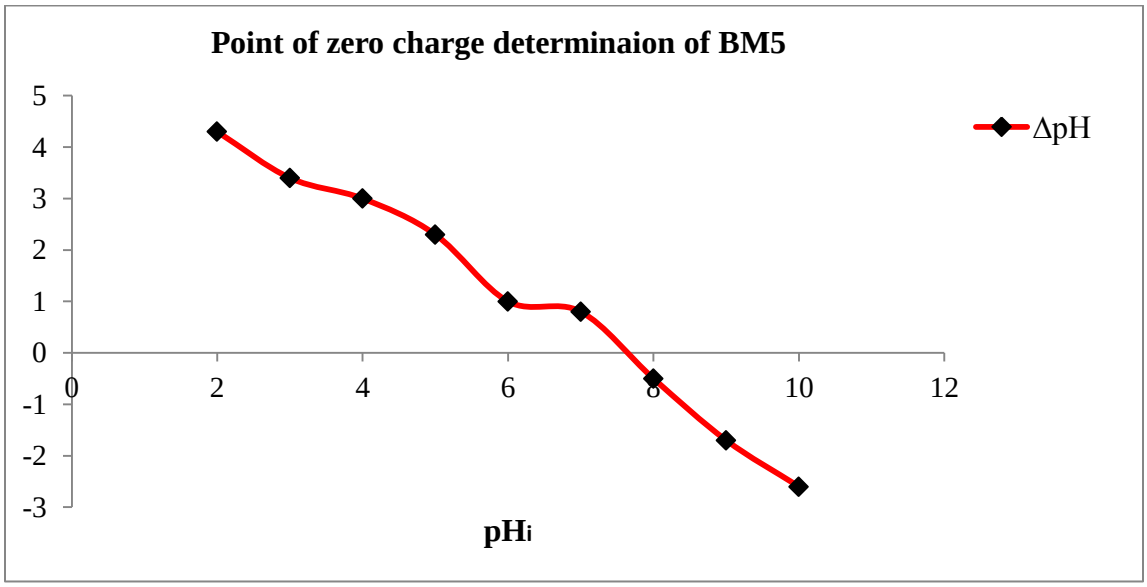



Figure 4.2 pH of point of zero charge (PHpzc) for base modified AC@ 500 $^{o}$C (BM5)

From figure 4.2 it can be seen that $pH_{PZC}$ is located at pH of 7.8; this indicates that anion adsorption is enhanced at pH less than 7.8, while pH of greater than 7.8 is preferable for cationic adsorptions (Salleh *et al.*,, 2011). Hence, at pH > PZC the adsorbent surface is negatively charge which favored the adsorption of the positively charged GY 28 dye molecules maybe due to the strong electrostatic attraction between the negatively charged BM5 surface and the positively charged GY 28 dye molecules leading to maximum adsorption of dye at high pH. So, GY 28 dye adsorption onto BM5 is favored at pH higher than 7.8 (i.e pH > 7.8). Therefore base modified AC effectively works at high pH of the dye solution.

### 4.3.4 XRD analysis

The crystalline structure of the prepared activated (BM5) was characterized by powder X-ray diffraction (XRD). X-ray diffracts grams for all the activated carbon is show in figure 4.3. The XRD spectra of the activated carbon illustrated the presence of different alumino silicate minerals. From Figure 4.3, the structure of BM5 is cellulose based through XRD pattern (the broaden peaks at $2\theta = 21.78^{o}$ which refer to cellulose structure, secondary peaks at $2\theta=15.32^{o}$ to polysaccharide structure. In this study the XRD analysis of the two peaks which reflects the stacking of degree of aromatic carbon sheets on the BM5 activated carbon. This study supported by Zhao *et al.*, 2014 showed that the main crystallite structure of BM5 was stable even after base modification with a little intensity difference.

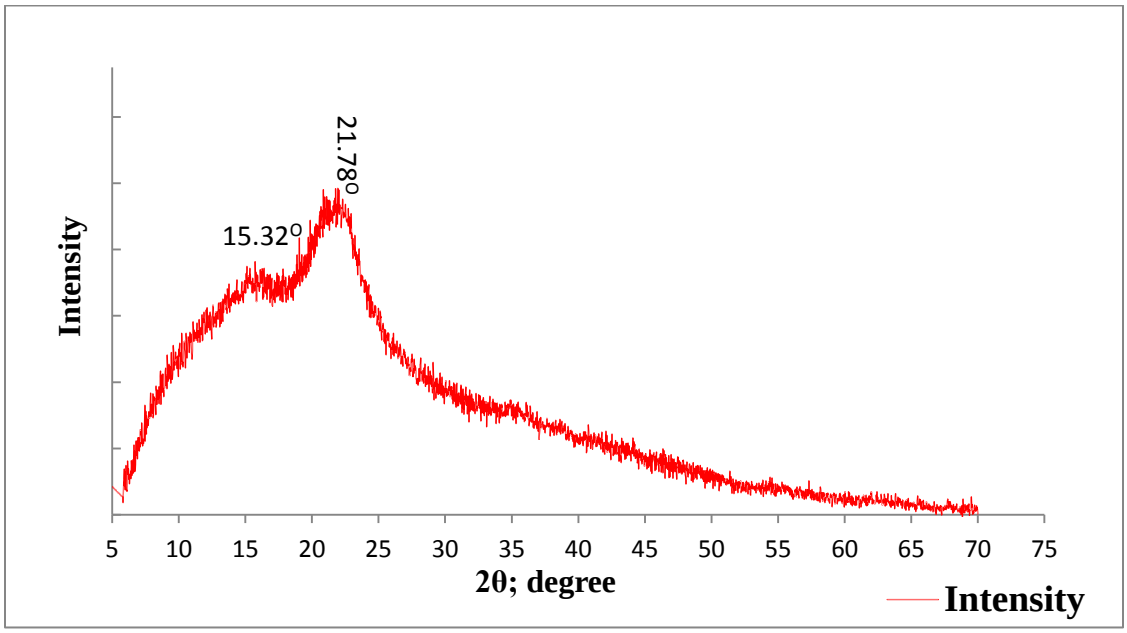



Figure 4.3 XRD pattern of BM5 activated carbon

The XRD analyses were performed for modified PS sample before and after adsorption see Figure 4.3. All characteristics peaks are highly consistent with the simulated pattern for base modified activated carbon (BM5) and pattern for loaded BM5.The crystallized structure of BM5 was stable after the adsorption by comparing XRD patterns for original and GY 28 dye loaded BM5.

### 4.3.5 FT-IR spectra Analysis

FTIR is one of the most frequently used instrumental analysis methods to characterize the surface functional groups in prepared activated carbons that might be involved in the binding of dye ions. The adsorption efficiency of prepared activated carbons like BM5 can be influenced by the chemical structure of the surface. It can be observed that for prepared samples functional groups related with the raw components of biomass exist. The infrared adsorption spectrums of raw PS, chemically modified PS (BM5) and also loaded one (LBM5) are shown in Figure 4.4 with in the region of 4000 - 400 $cm^{-1}$.

Raw Peanut Shells mainly consist of polysaccharides, proteins, and lipids, offering many functional groups such as carboxyl, carbonyl, hydroxyl and amino with characteristic chemical structures. The infrared vibrational spectra for RPS, the major intense bands were observed at 3423 $cm^{-1}$ represents the stretching vibration of the hydroxyl groups (−OH) this band related with hydrogen bonding possibly due to water is still remaining in the raw sample and also the interaction

and presence of alcoholic, phenolic, amino, and carboxylic derivatives (M. E. Ossman *et al.*, 2017). The peaks at 2932 $cm^{-1}$ assigned to (C−H) stretching vibration, characteristic of aromatics, aliphatic and olefins in the lignin. The peaks at 1648 $cm^{-1}$ represents carbonyl (−C=O) stretching vibration, attributed to carbonyl compounds such as, ketones, aldehydes alkenes, esters and C = C of aromatic groups; at 1385 $cm^{-1}$, possibly due to C−O, N=O or C−C stretching vibrations. The observed peaks at 1042 $cm^{-1}$ was due to the C−O group in carboxylic and alcoholic groups. The peak at 568 $cm^{-1}$ is due to the vibrational bending in the aromatic compounds of lignin. Some of the above mentioned functional groups are typical of lignin, which is present in different agricultural byproducts and wastes like peanut shell (Chen *et al*., 2015) and also see Table 4.7 and appendix C.

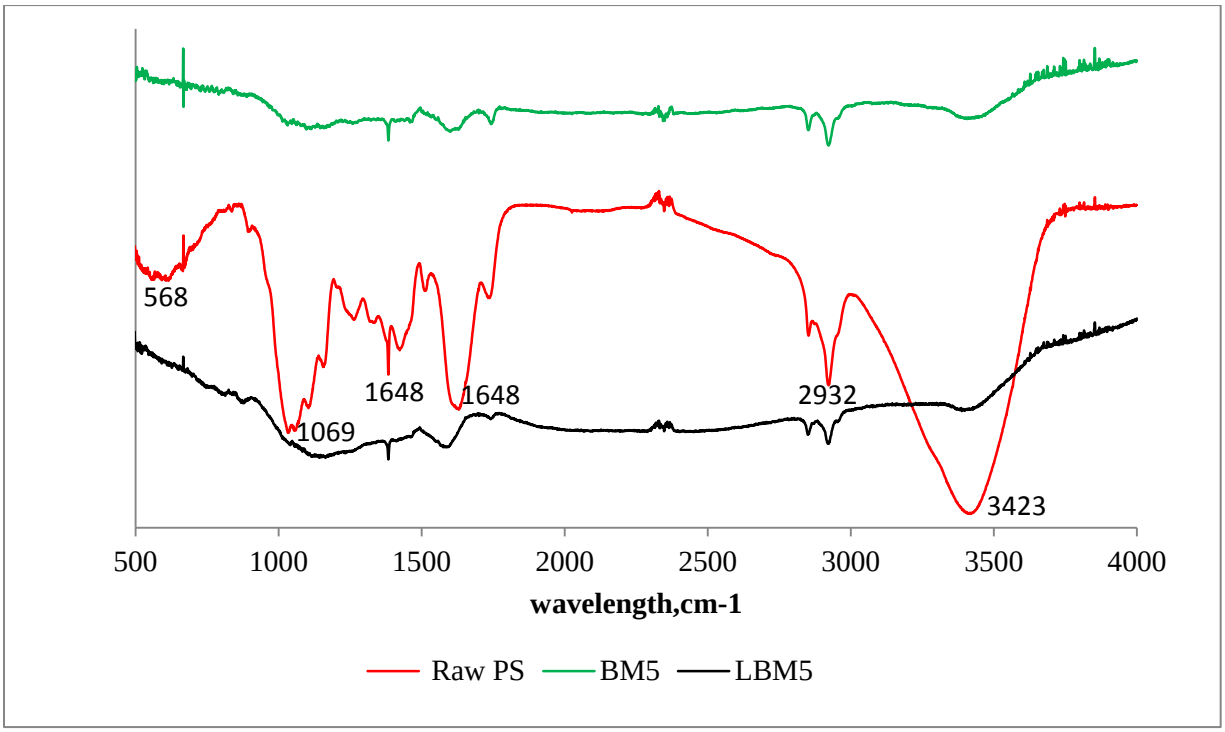
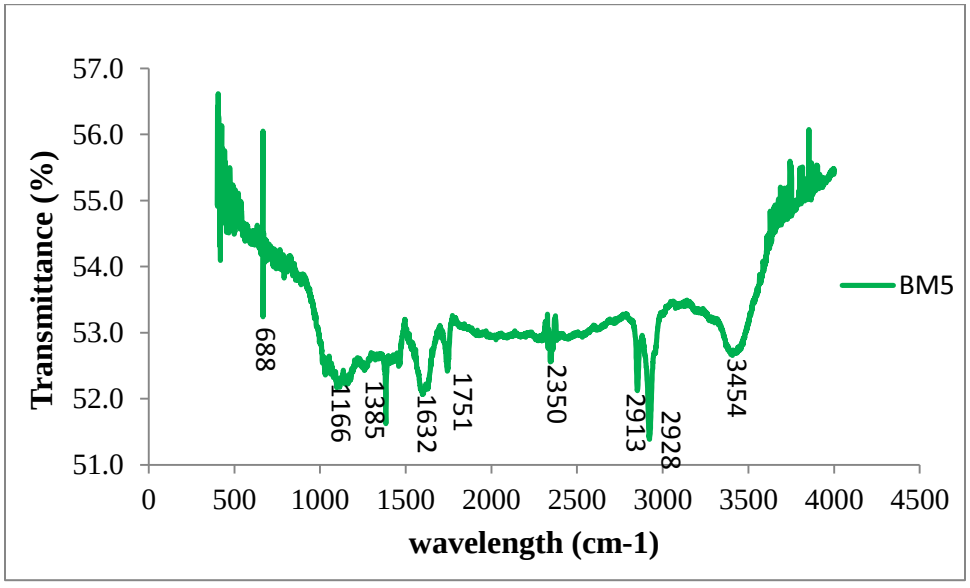



Figure 4.4 FTIR analyses for raw peanut shell, BM5 and LBM5

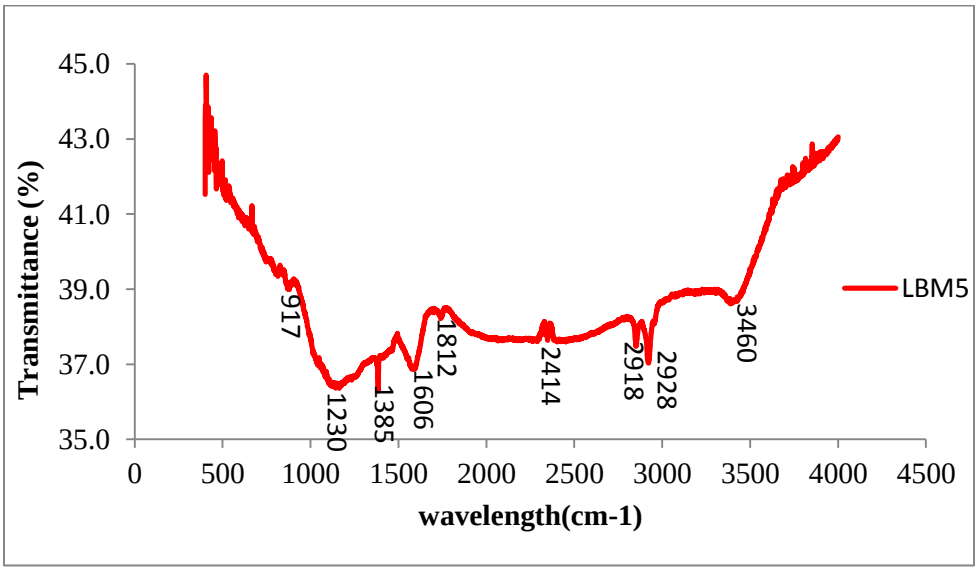
The comparison of the spectrum between the RPS and also BM5 before adsorption show a little similar infrared peaks; however, some changes have occurred in peak intensity due to the chemical activation stage see Table 4.7. But some of functional groups changed in the activated samples like BM5, which may also be beneficial for the adsorption process.

Table 4.6 FT-IR analysis of the BM5 activated carbon sample

| Frequency; wavelength($cm^{-1}$) | Absorption band | Functional group |
|---|---|---|
| 688 | C-C, C-H and O-H | Out of plane bending mode of Hydroxyl and Methyl |
| 1166 | C-O stretch | Conjugated Ester |
| 1385 | C-O stretch and N=H bend | Ester and Nitro |
| 1632 | C-O stretch with Aromatic | Carboxyl |
| 1751 | C=C | Ketones |
| 2350 | C-N stretch | Nitriles |
| 2913 | C-H stretch | Methyl and Methylene |
| 2928 | C-H stretch | Methyl and Methylene |
| 3454 | O-H and N-H stretch | Hydroxyl, Phenols & alcohols and Amines $1^{o}$&$2^{o}$ |




(a)




(b)

Figure 4.5 FTIR analyses for (a) before (BM5) and (b) after (LBM5) adsorption

The peaks in the FT-IR spectrum on Figure 4.5(a) for BM5 prior to adsorption were represented to various groups and bands in accordance to their respective wave numbers ($cm^{-1}$) showing the complex nature of the adsorbent. Therefore from the figure 4.5(b) show, those functional groups like carbonyl, hydroxyl, amino and nitriles groups were more responsible for the adsorption process of the removal of GY 28 dye from the solution due to the change of peaks at 688, 1166, 1632, 1751, 2350 and 3454 $cm^{-1}$ on BM5 activated carbon. Many researchers have shown the significance of the analysis of the FTIR spectrum analysis with respect to the presence of ionizable groups (carboxyl and hydroxyl) able to interact with negative or positive dye ions (Gong *et al.*, 2005; Song *et al.*, 2011).

Table 4.7 FT-IR analysis of the cellulose, hemicellulose and lignin components (Chen *et al.*, 2015;Yang, 2007)

| Range of Wavenumber,$cm^{-1}$ | Absorption band |
|---|---|
| 3460-3412 | O-H stretching |
| 3000-2842 | C-H stretch in methyl and methylene group |
| 2860–2970 | C–$H_n$ stretching with Alkyl, aliphatic, aromatic |
| 1738-1709 | C-O stretch in unconjugated ketone, carbonyl and ester groups |
| 1675-1655 | C=O stretching in conjugated. Aryl ketones |
| 1605-1593 | Aromatic skeleton vibrations plus C-O stretching |
| 1515-1505 | Aromatic skeleton vibrations |
| 1470-1445 | C-H deformations (asym in -$CH_3$ and -$CH_2$ ) |
| 1430-1422 | Aromatic skeleton vibrations combined with C-H in plane de-formations |
| 1370-1365 | Aliphatic C-H stretching in $CH_3$ and phen. OH |
| 1270-1266 | Ring plus C + O stretching |
| 1233-1214 | C-C + C-O + C=O stretching |
| 1166 | Typical for lignin; C-O in ester groups (conj.) |
| 1140 | Aromatic C-H in-plane deformation |
| 1128-1125 | Typical secondary alcohol and C-O |
| 1110 | Aromatic C-H deformation |
| 1086 | C-O deformation in sec. alcohol and aliphatic ether |
| 1035-1030 | Aromatic C-H in-plane deformation plus C-O deform. in primary alcohols plus C-H stretching (unconjugated) |
| 990-966 | -HC=CH- out -of-plane deform (trans) |
| 925-915 | C-H out of plane (aromatic ring) |
| 895-885 | C-H deformation vibration; $CH_2$ wagging |
| 858-817 | C-H out of plane in different positions |
| 700–400 | C–C, C-H and O-H stretching with Out of plane bending mode of Hydroxyl and Methyl |

### 4.4 Effects of Process Variables on adsorption efficiency

Adsorption of dye onto the surface of a prepared AC material is affected by several factors, such as pH, initial dye concentration, contact time and dosage of adsorbent. Before that we were presented the calibration carve show in figure 4.6.

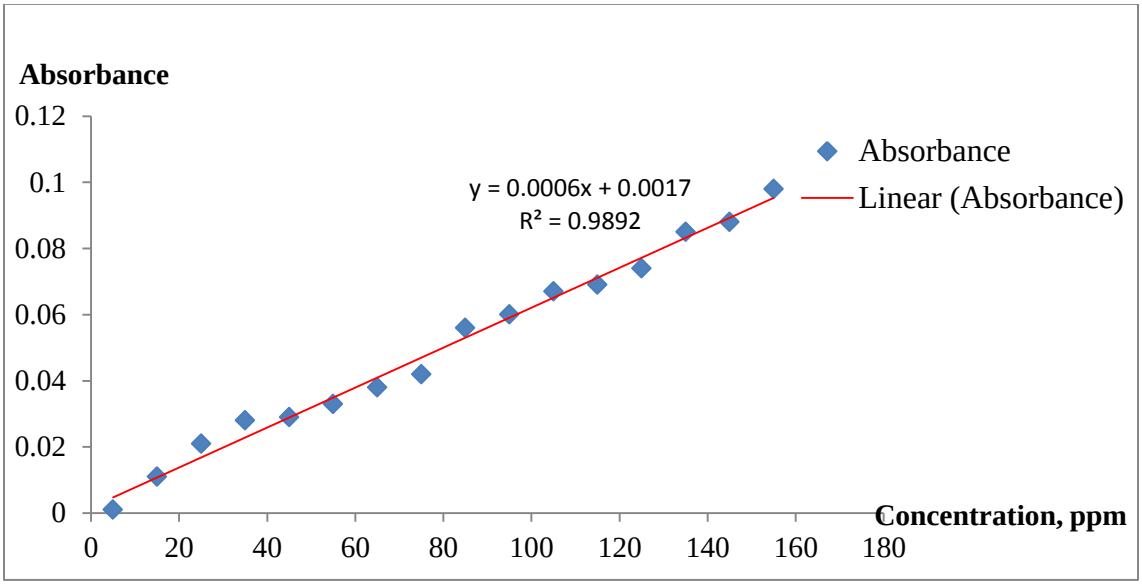



Figure 4.6 GY 28 Dye calibration carve

#### 4.4.1 Effect of pH

Solution pH is one of the most critical parameters in the adsorption process and contaminant removal from aqueous solutions. It is well-known that pH can affect protonation of functional groups (i.e. carboxyl, phosphate and amino groups) in the biomass, as well as the chemistry of the dyes (i.e. its solubility)(Mane & Babu, 2011). As shown in Figure 4.7, In the case of BM5 and Bi-Ch5 prepared activated carbon the dye uptake increased with the increasing pH in the range of 1.5 to 10. At pH 10, sorption efficiency achieved maximum values; 86.7% and 48.5% respectively at initial concentration of 100 ppm, 0.5 gram of adsorbent dose after 60 min of contact time respectively. It can be seen in figure 4.7 that as the solution pH increases, the adsorption efficiency increases in both cases. For both adsorbents the maximum adsorption efficiency was attained at a pH of 10.

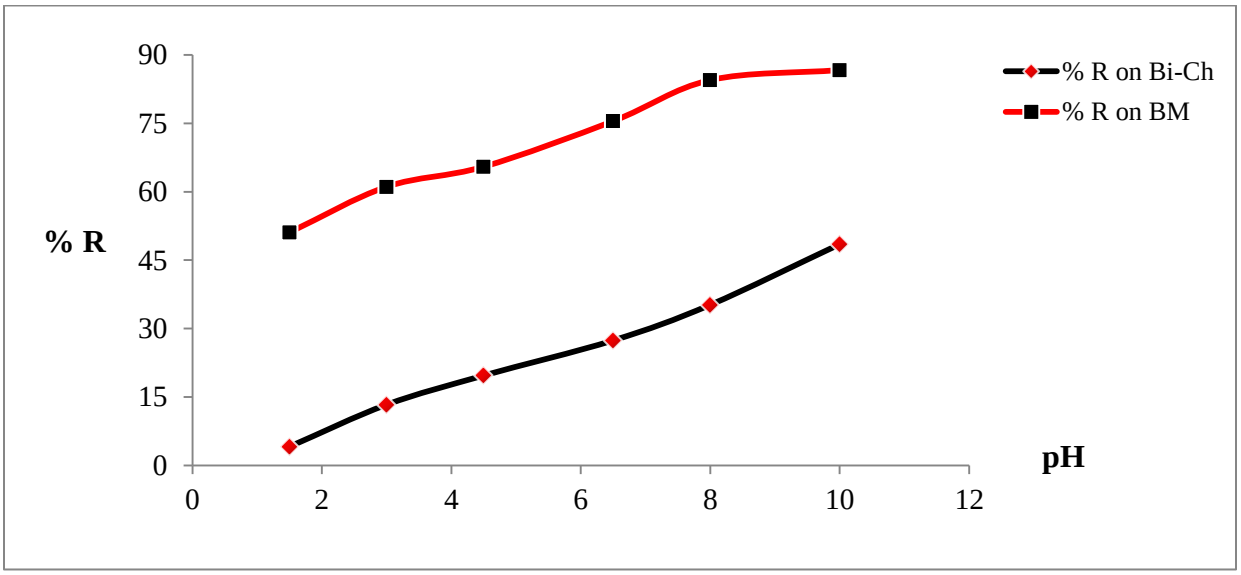



Figure 4.7 Effect of pH on % removal of dye by Bi-Ch5 and BM5 prepared activated carbon (@ $C_o$= 100 ppm, t= 60mit, $D_o$= 0.5 gm, agitation speed 150 rpm and $T^o$= 25±5 $^oC$ )

At high pH solution, the positive charge at the solution interface decreases and the adsorbent surface appears negatively charged. As a result, the cationic dye adsorption increases and anionic dye adsorption shows a decrease (Salleh *et al.*, 2011). So for this study at high pH values, the $OH^-$ concentration in the solution is high and the adsorbent surface makes negatively charged. Consequently, GY 28 dyes, which are positively charged, are attracted for the adsorbent surface. At lower pH, sorbed amount of GY 28 dye decreased because the surface area of the adsorbent was more protonated and a competitive sorption occurred between $H^+$ protons and positively charged GY 28 dye at the surface sites. Therefore, $H^+$ ions react with the anionic functional groups on the surface of Bi-Ch5 & BM5 and results on a reduction of the number of binding sites available for the sorption of GY 28 dye. On the basis of the present results, the value of pH 10.0 was selected as an optimum pH for the further experimental studies. The maximum adsorption capacity was found to be 26 mg/gm and 14.58 mg/gm for BM5 and Bi-Ch5, respectively at an optimum condition.

### 4.4.2 Effect of Initial Dye Concentration

The percentage removal efficiency of dye is highly dependent on the initial amount of dye concentration. As presented in figure 4.8, when the initial GY 28 dye concentration was increased from 30 to 150 ppm, with a constant 100 ml of dye solution and 0.5 gm of adsorbent at 60 min

results show that the percentage of dye removal efficiency decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. The effect of the initial of dye concentration factor depends on the relation between the concentration of the dye and the available binding sites on an adsorbent surface (Salleh *et al.*, 2011). Figure 4.8 showed maximum removals efficiency of dye with 30 ppm which indicates a high degree of affinity of the interacting groups on the surface of the prepared activated carbon BM5 and Bi-Ch5 with 72.3% and 56.7% respectively. But the adsorption capacity of BM5 directly proportional to the initial GY 28 dye concentration; so the equilibrium adsorption capacity of the biomass increased with increased in the initial dyes concentration; this was due to the higher adsorption rate and the utilization of all available active sites for adsorption at higher dyes concentration. Increasing of adsorption capacity occur as a result of high driving force for mass transfer at a high initial dye concentration. Therefor in this study; the maximum adsorption capacity was found to be 17.37 mg/gm and 15.26 mg/gm for BM5 and Bi-Ch5, respectively at high concentration; 150ppm.

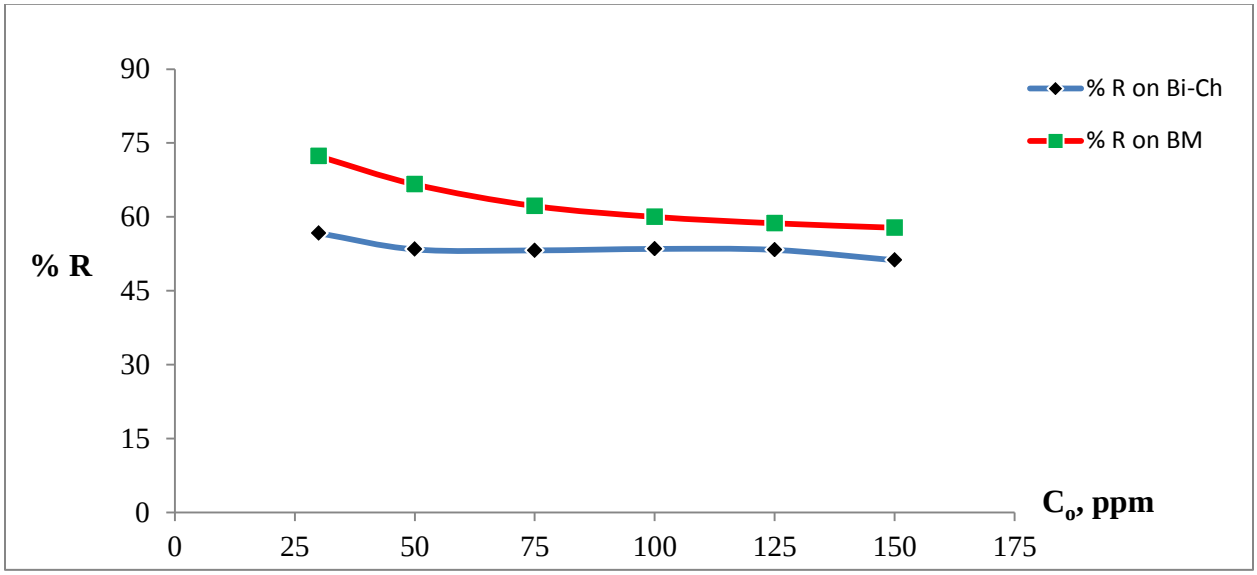



Figure 4.8 Effect of initial dye concentration of the solution on Bi-Ch and BM @ 500 $^oC$ activated carbon (@ pH= 7, t = 60mit, $D_o$= 0.5 gm, V= 100ml, 150 rpm and $T^o$= 25±5 $^oC$ )

### 4.4.3 Effect of Contact Time on Dye Removal

Contact time can be effective on adsorption processes. In adsorption processes, contact time influencing mechanism involves the migration of dye from bulk of the solution to the surface of

the adsorbent and diffusion of dye through the boundary layer to the surface and into the interior pores of the adsorbent (Abbas *et al.*, 2012). As presented in Figure 4.9, for a fixed initial 150 ppm concentration of GY 28 dyes with 100ml of dye solution at pH 10 and a fixed adsorbent mass 0.5g; the results show an increase in the adsorption removal efficiency and adsorption capacity as the time of contact increases. This is understandable because of the existence of equilibrium for the process of adsorption, the process will continue until all active sites (pores) are filled with dye molecules. In addition, the adsorption process was fast at the beginning due to availability of large area then the process will slow down as more pores are filled by molecules. Figure 4.9 shows that the adsorption rate increased rapidly and that the maximum removal efficiency and adsorption capacity were reached 60 min: 52.2 % and 15.67 mg/gm on Bi-Ch5 and 83.3 % and 25 mg/gm on BM5, for GY 28 dyes solution.

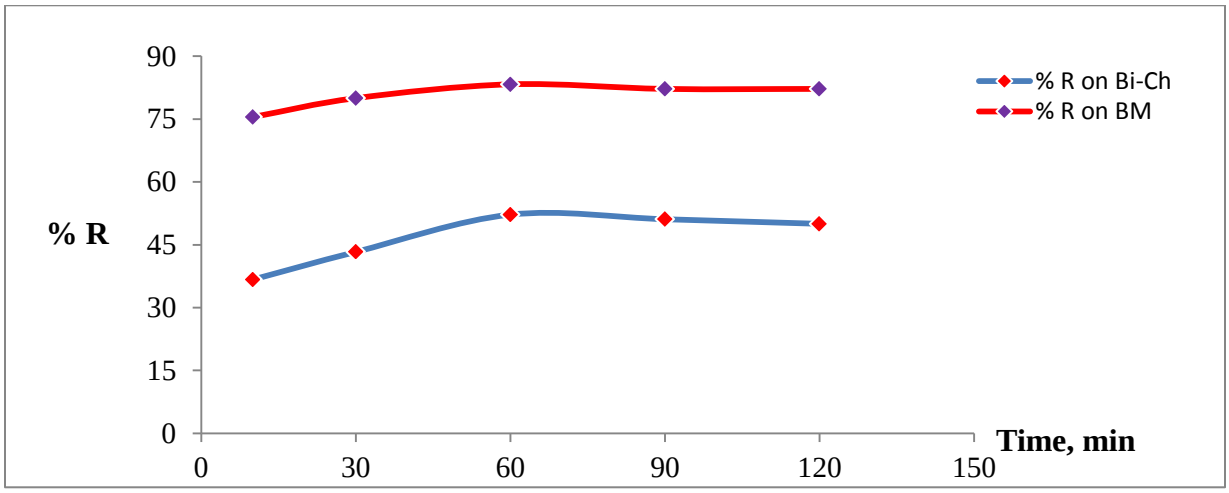



Figure 4.9 Effect of contact time on the adsorption processes by Bi-Ch and BM @ 500 $^{o}$C activated carbon (@ pH=10, $C_o$= 150 ppm, $D_o$= 0.5 gm, rpm =150 and $T^o$= 25±5 $^{o}$C)

### 4.4.4 Determination of Equilibrium Time

The equilibrium time is the time at which the process reaches equilibrium. The equilibrium time should be known because it can help us in determining the residence time for an adsorption process. Generally equilibrium time means the rate of adsorption of molecules on to the surface becomes similar to the rate of desorption from the surface.

Determination of equilibrium time for the adsorption process was done by carrying the process for longer periods of time i.e. 10 min, 30 min, 1, 1.3, 2, 3, 4 and 24 hrs at concentration of 150

ppm, with 0.5g adsorbent dose and pH of 10. As presented in Figure 4.10, the removal efficiency of GY 28 dyes increased from 63.3% to 83.3% up to 2 hrs and remains constant 24 hrs later with maximum removal of for GY 28 dye. Therefore, equilibrium time of 2 hrs was selected for the adsorption of GY 28 dye for further studies.

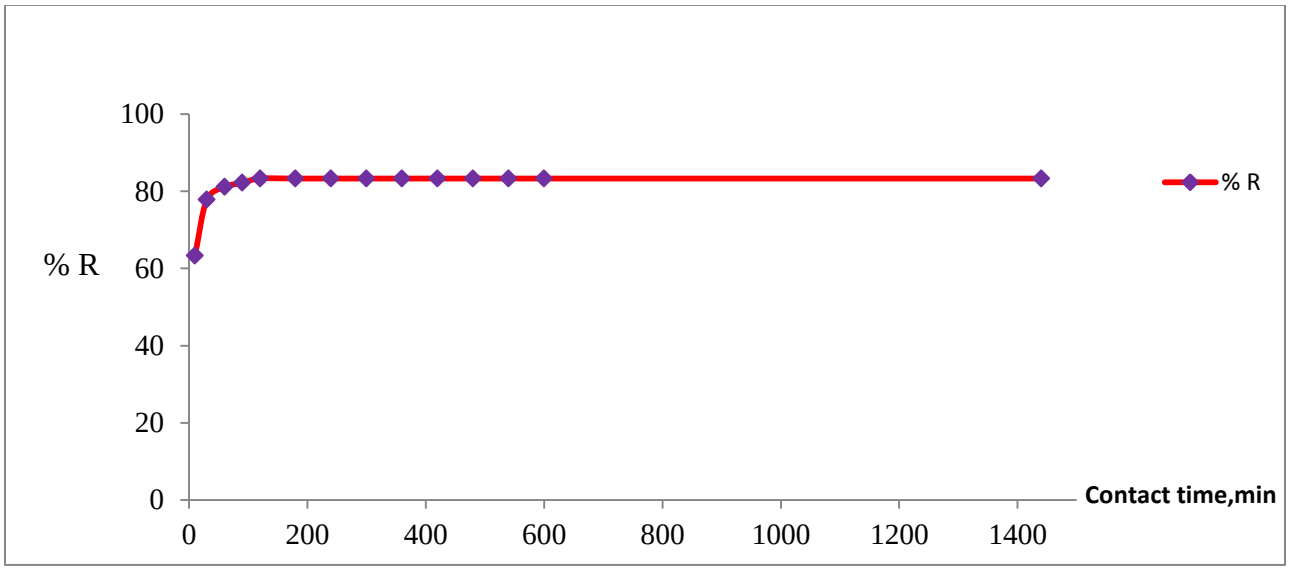



Figure 4.10 The equilibrium time for GY 28 dye adsorption on BM5 (@ V=100ml, pH=10, $C_o$= 150 ppm, $D_o$= 0.5 gm, rpm =150 and $T^o$= 25±5 $^oC$)

### 4.5 Data analysis using Design Expert software 6.0.8

#### 4.5.1 Data analysis using General full factorial

General full factorial was established with Design Expert 6.0.8 software for statistical design of experiment and data analysis. Effect of concentration, pH, and contact time on the adsorption removal efficiency was analyzed using Design-Expert 6.0.8 software in order to determine the significant of the model and the factors. Adsorption removal efficiency obtained from the experiment work was an input data for the software.

The optimum conditions for GY 28 dye adsorption onto BM5 were predicted by the quadratic model of the response surface methodology (RSM). The interaction between independent (process) variables and dependent variables (responses) were analyzed by ANOVA. The quality of fit polynomial model was expressed by $R^2$ and its statistical significance was examined by the F-test. Model terms were evaluated by the P-value (probability) with 95% confidence level.

The significance of the model was justified by the analysis of variance (ANOVA). The ANOVA summary for GY 28 dye is given in Table 4.8 the analysis was done by means of Fisher's 'F'-test. The model F-value observed was 17.02 implies that the model was significant. The parameters having an F-statistics probability value less than 0.05 are said to be significant. In this present study the probability of model F statistics value was <0.0001 indicating that the model suggested by the software was highly significant. In this case A, B, $B^2$, and $C^2$ are statistically significant ($P<0.05$) model terms at the 95 % confidence level.

Table 4.8 Analysis of variance (ANOVA) for removal efficiency of GY 28 dye

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | |
|---|---|---|---|---|---|---|
| Model | 2636.20 | 9 | 292.91 | 17.02 | <0.0001 | significant |
| A | 1369.39 | 1 | 1369.39 | 79.55 | <0.0001 | |
| B | 510.93 | 1 | 510.93 | 29.68 | <0.0001 | |
| C | 19.43 | 1 | 19.43 | 1.13 | 0.3029 | |
| $A^2$ | 51.24 | 1 | 51.24 | 2.98 | 0.1026 | |
| $B^2$ | 334.01 | 1 | 334.01 | 19.40 | 0.0004 | |
| $C^2$ | 253.93 | 1 | 253.93 | 14.75 | 0.0013 | |
| AB | 50.02 | 1 | 50.02 | 2.91 | 0.1065 | |
| AC | 4.69 | 1 | 4.69 | 0.27 | 0.6085 | |
| BC | 42.56 | 1 | 42.56 | 2.47 | 0.1343 | |
| Residual | 292.63 | 17 | 17.21 | | | |
| Lack of Fit | | 17 | | | | |
| Pure Error | | 0 | | | | |
| Cor total | 2928.83 | 26 | | | | |

A= pH, B= Concentration, C= Time

### 4.5.2 Model analysis and Regression modeling

The dye removal efficeny of BM5 from aqueous solution on the interaction of three process factors (pH (A), initial dye concentration (B), and contact time (C)) were used for the model generation. The output of different model summary statistics, shown in Table 4.9, focus on obtaining larger adjusted R-Squared and the predicted R-Squared values so that model accuracy can be maximized. Therefore, quadratic model is suggested for model generation. Moreover, as

shown in the Table 4.9, for GY 28 dye, The "Pred R-Squared" of 0.7420 is in reasonable agreement with the "Adj R-Squared" of 0.8472. The quadratic model developed for the responses was found to be significant with p-value less than 0.0001. High squared correlation coefficients ($R^2$) of 0.9001 was obtained for removal efficiency of GY 28 dye; thus ensuring a satisfactory agreement of the second-order regression model with the experimental results. Based on the results, the response surface model constructed in this study for predicting GY 28 adsorption was considered adequate.

Table 4.9 Model summary statistics

| Source | Std. Dev | R-Squared | Adjusted R-Squared | Predicted R-Squared |
|---|---|---|---|---|
| Liner | 6.69 | 0.6486 | 0.6028 | 0.5247 |
| 2FI | 6.83 | 0.6818 | 0.5864 | 0.4762 |
| Quadratic | 4.15 | 0.9001 | 0.8472 | 0.7420 |

Regression analysis for the selected independent variables was conducted using ANOVA to determine statistically significant effects. Regression analysis was performed to fit the response functions, i.e. GY 28 dye percentage removal efficieny by BM5. An empirical relationship between the response and the input test variables in actual units can be expressed by the following equation:

**Adsorption Removal Efficiency** = 65.30 + 8.72 * pH + 5.33 * concentration + 1.04 * Contact time - 2.92 * $(pH)^2$ + 7.46 * $(Concentration)^2$ - 6.51 * $(Contact\ time)^2$ + 2.04 * (pH * Concentration) - 0.63 * (pH * Contact time) + 1.88 (Concentration * Contact time); this equation represents in case of final Equation in Terms of Coded Factors.

Similarly final equation in terms of actual factors was expressed as follow;

**Adsorption Removal Efficiency** = 42.90333 + 4.78367 * pH - 0.64150 * Concentration + 0.81517 * Contact time - 0.23855 * $(pH)^2$ + 2.98444E(-003) * $(Concentration)^2$ - 7.22840E(-003) *$(Contact\ time)^2$ + 0.011667 * (pH * concentration) - 5.95238E(-003) * ( pH * Contact time) + 1.25556E(-003)* (Concentration * Contact time)

The coefficients for the quadratic terms for GY 28 dye adsorption onto BM5 were shown to be significant. This indicates that these factors influence the % removal efficiency of GY 28 dye.

### 4.5.3 Interaction effects of process variables on adsorption performance of BM5 AC

The best combination of variables where all parameters meet the desired removal criteria could be graphically determined. The feasible response terms that fit the optimization criteria would be graphically shaded in order to obtain the optimum zone.

#### 4.5.3.1 Interaction effects of process variables on adsorption of GY 28 dye

The interaction effect of concentration and time is increasing the the removal efficeny on BM5 as both parameters increase with constant pH of 10, as shown in Figure 4.11(a). The effect of increasing the concentration on the % removal show a pronounced increase than time. The maximum persentage removal of 85.48 % was obtained at time of 58.55 min and 149.27 ppm concentration while the minimum removal efficiency is obtained at pH 3, 46.06% at 30.54 min and 106 ppm concentration for GY 28 dye.

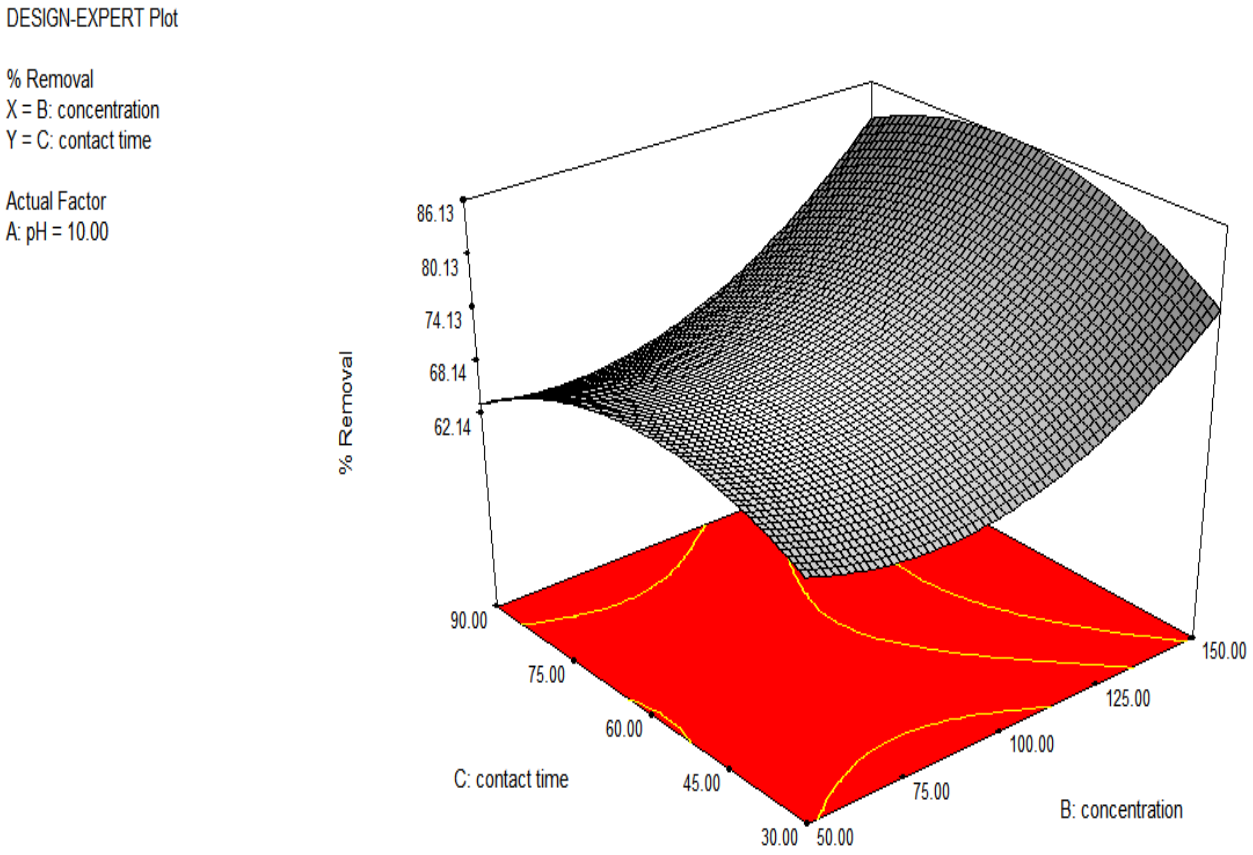



Figure 4.11 a) Interaction effect of concentration and time at a constant pH 10

The effect of pH and time was also shown in Figure. 4.11(b) at constant concentration of 150 ppm. The result can be explained as increasing both time and pH improves the % removal but the

contribution of time is more significant than pH in comparison. The maximum % removal is observed at time 64.29 min and alkaline condition pH 9.80, it has a value of 85.62% while the minimum % removal is obtained 50.43% at pH 3 and 90 min with initial 53.67 ppm concentration .

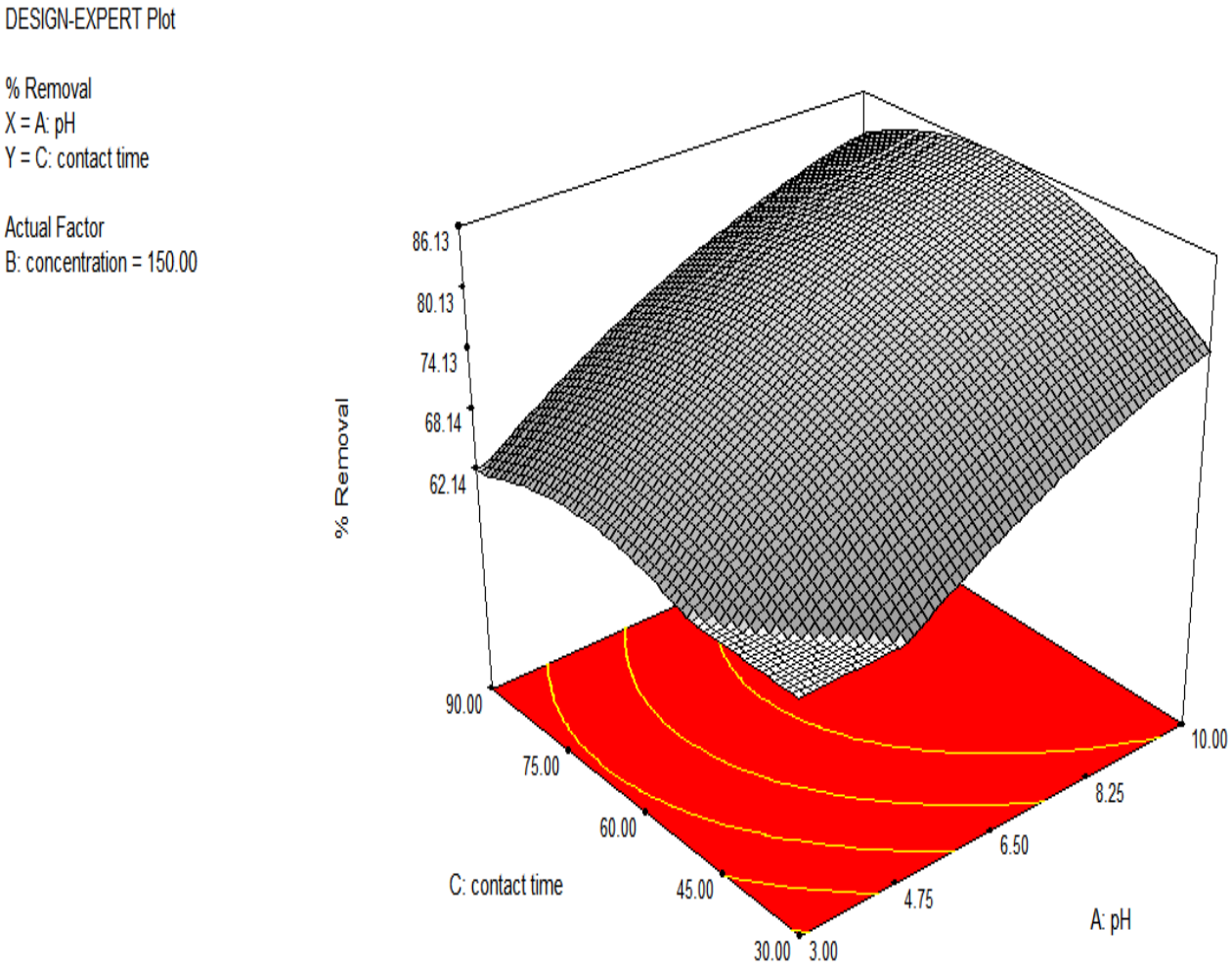



Figure 4.11 b) Interaction effect of contact time and pH at constant concenetration 150 ppm

The interaction effect of pH and concentration was seen in Figure 4.11 (c) at constant time of 60 min. The result indicates that increasing both concentration and pH improves the % removal but the contribution of concentration is more significant than pH. The maximum value was observed when solution pH is 9.88 and concentration is 147.12 ppm, 84.5 % while the minimum is obtained at pH 3 and 50 ppm concentration, 57.83%.

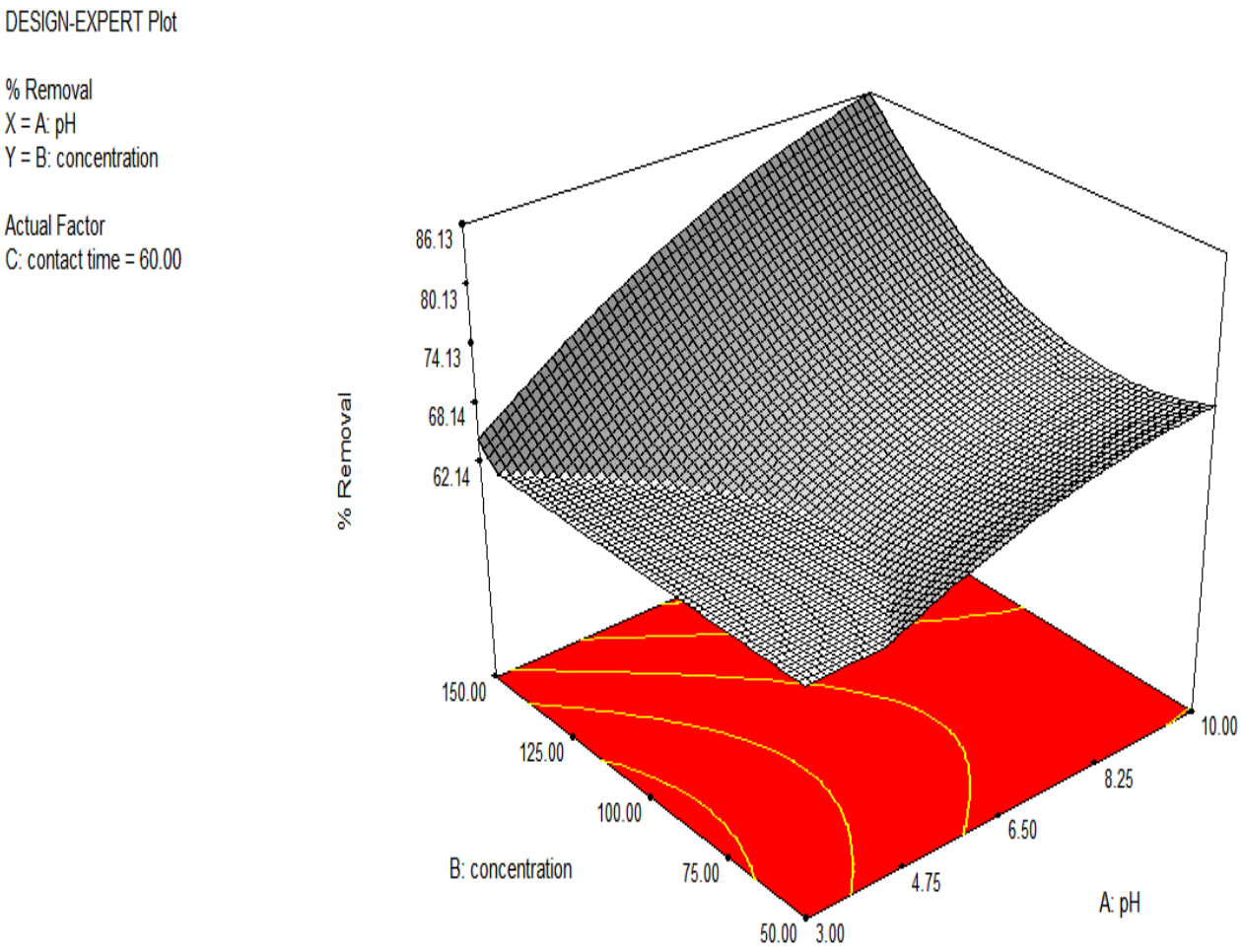



Figure 4.11 c) Interaction effect of pH and concentration at constant time 60 min

Figure 4.11 ( a, b and c) Interaction effects of process variables on % removal (3D surface plot) for GY 28 by BM5

### 4.5.4 Model adequacy test using ANOVA

The adequacy of the model was also justified by the analysis of variance (ANOVA) show in Table 4.10. The fitting of the experimental data to the regression model was checked and suitably explained by the value of the adjusted determination coefficient (Adj R-Squared = 0.8472). This result means that 0.0241%? of the total variation on GY 28 dye adsorption data can be explained by the selected model. The adequate precision ratio of 16.02 for GY 28 dye, indicates an appropriated signal to noise ratio. The ratio determined was greater than 4, representing that the quadratic model can be used to navigate the design space of this process.

Table 4.10 ANOVA result for significant response surface quadratic model terms

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | |
|---|---|---|---|---|---|---|
| Model | 2636.20 | 9 | 292.91 | 17.02 | <0.0001 | significant |
| A | 1369.39 | 1 | 1369.39 | 79.55 | <0.0001 | significant |
| B | 510.93 | 1 | 510.93 | 29.68 | <0.0001 | significant |
| $B^2$ | 334.01 | 1 | 334.01 | 19.40 | 0.0004 | significant |
| $C^2$ | 253.93 | 1 | 253.93 | 14.75 | 0.0013 | significant |
| Residual | 292.63 | 17 | 17.21 | | | significant |
| Lack of Fit | | 17 | | | | significant |
| Pure Error | | 0 | | | | |
| Cor total | 2928.83 | 26 | | | | |

$R^2$ = 0.9001; $R^2$ adj = 0.8472; Adeq. Prec. = 16.02;

The suitability of the selected model to approximate the real system was evaluated using the diagnostic plots. Studentized residuals represent normal distribution of residual points on a straight line. However, some scattering occurs even in normal data. Furthermore, as shown in Figure 4.12 for GY 28 dye, the relationship between actual values and predicted values showed that the actual values are distributed relatively near to the straight line, indicating good fitness of the model for GY 28 dye. The normal probability plot for the studentized residuals in Figure 4.13 is linear and evenly distributed.

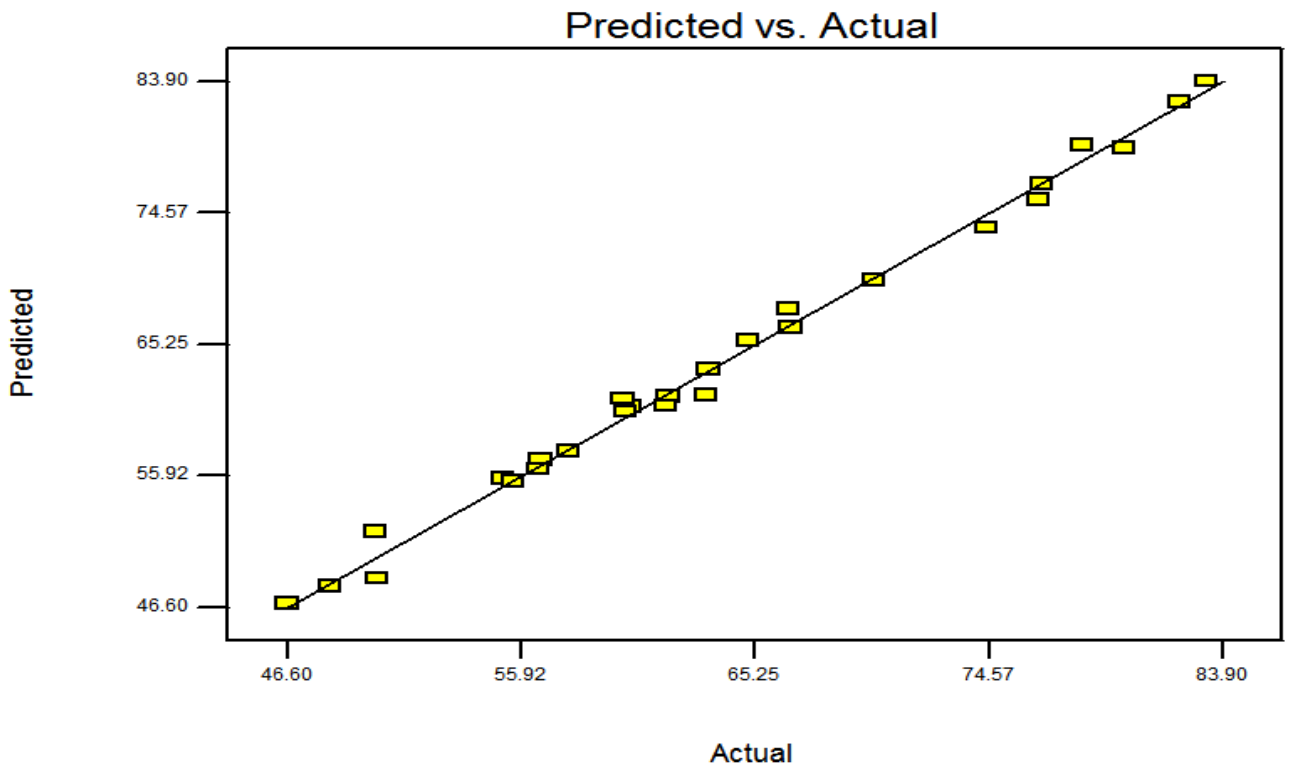



Figure 4.12 Predicted vs. Actual values for GY 28 Dye

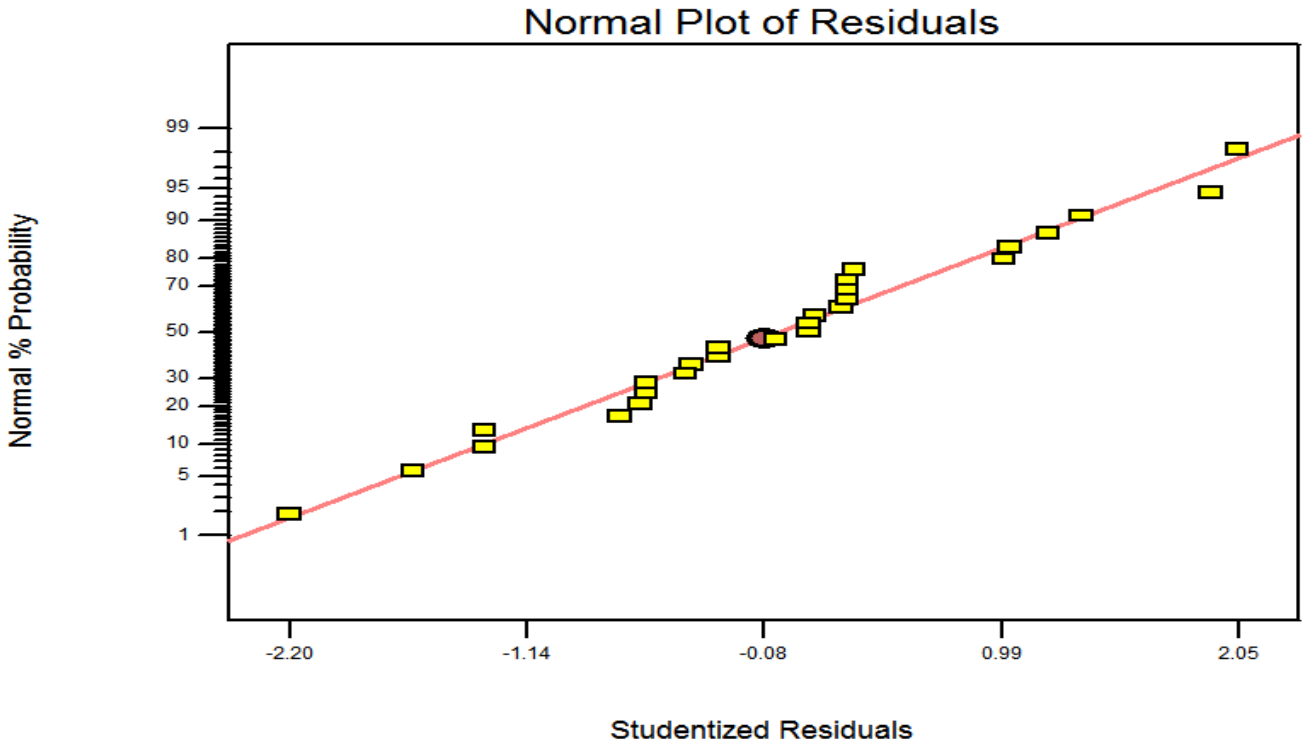



Figure 4.13 Normal % P vs. Studentized Residuals for GY 28 Dye

Again in Figure. 4.14, the plot of studentized residuals versus run order was tested and the residuals were scattered randomly around ±3.00. This was an indication of better fitment of the model with the experimental data.

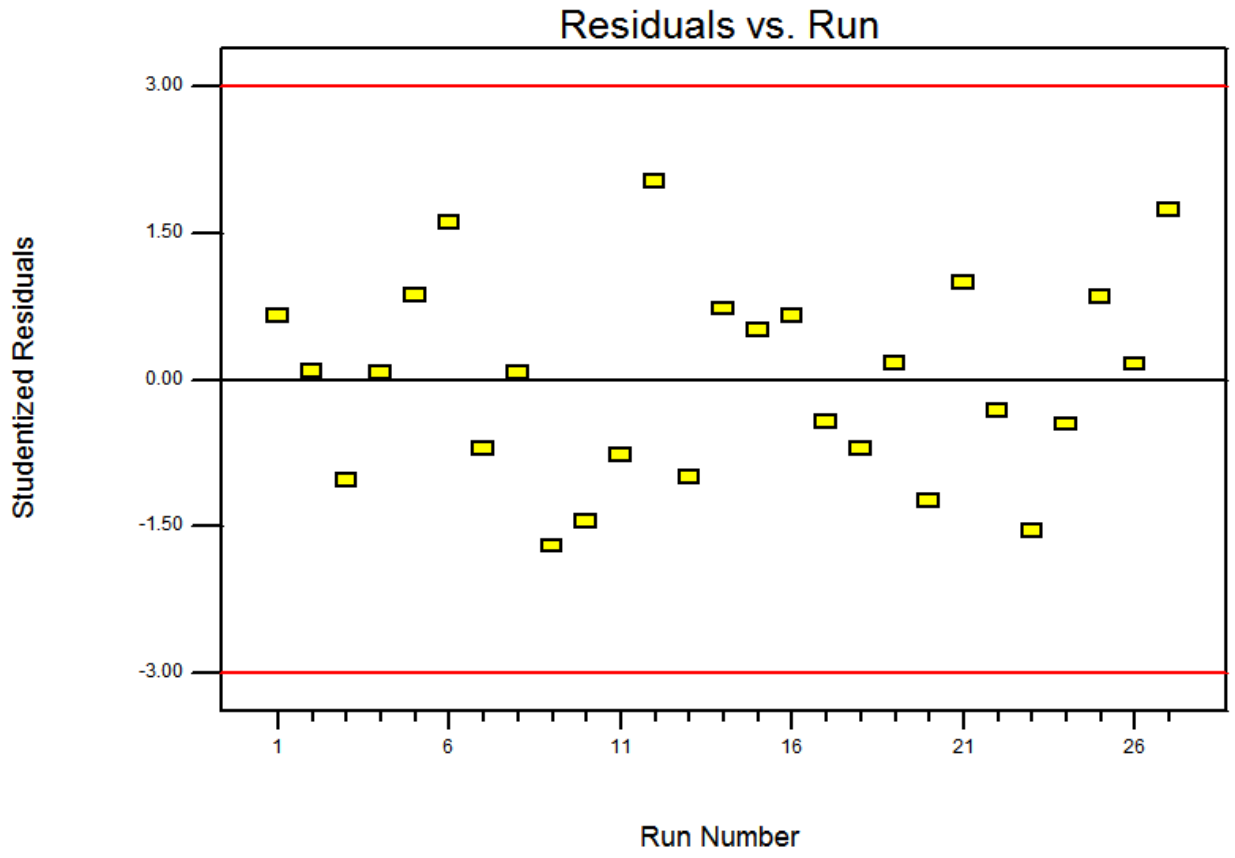



Figure 4.14 Residuals vs. Run values for GY 28 Dye

### 4.5.5 Response Optimization

The experimental design and response surface analysis as an efficient tool for the development and optimization of the processes. Response optimization is a method of analysis to identify the combination of input variable settings that jointly optimize a single response or a set of responses. The general model in ANOVA was used to identify the significant factors among the given factors. Within a statistical analysis program, the response optimizer function provides an optimal solution for the input variable combinations, and sometimes an optimization plot. The optimization plot may be interactive, in which case the input variable settings can be adjusted on the plot to search for more desirable solutions. In this study, the maximum adsorption removal efficiency

was specified as the response, and pH, time and initial dye concentration were provided as the factors. Based on the given factor's criteria, pH in maximum for initial concentration and contact time interaction and contact time at 60 mint for Co, ppm and pH interaction with in the give range, the Figure 4.11(a, b and c) shows the results of the response optimizer analysis indicates that the maximum % removal is 85.48%, 85.62% and 84.5% with a desirability of 1 respectively. When optimal conditions are selected from the above, the developed method is subjected to a validation procedure in case it will be used for quantitative purposes.

### 4.6 Adsorption Isotermal Analysis

Adsorption isotherms demonstrate the relationships between the adsorption capacity and the residual concentration of the adsorbate at constant temperature. it"s can be describe the distribution and interaction of dye molecules within the adsorbent at equilibrium. Several isotherm models are available; two most well-known models were selected for this study: Langmuir and Freundlich models, due to their simplicity and reliability and which provide information on the adsorption capacity and constants related to the activation energy. Analysis of the equilibrium data is significant to develop an equation which precisely represents the results and can be used for opti- mizing the design of an adsorption system. Linear regression is commonly used to determine the best fitting isotherm and the applicability of isotherm equations is compared by judging the correlation coefficients, $R^2$.

#### 4.6.1 Langmuir isotherm model

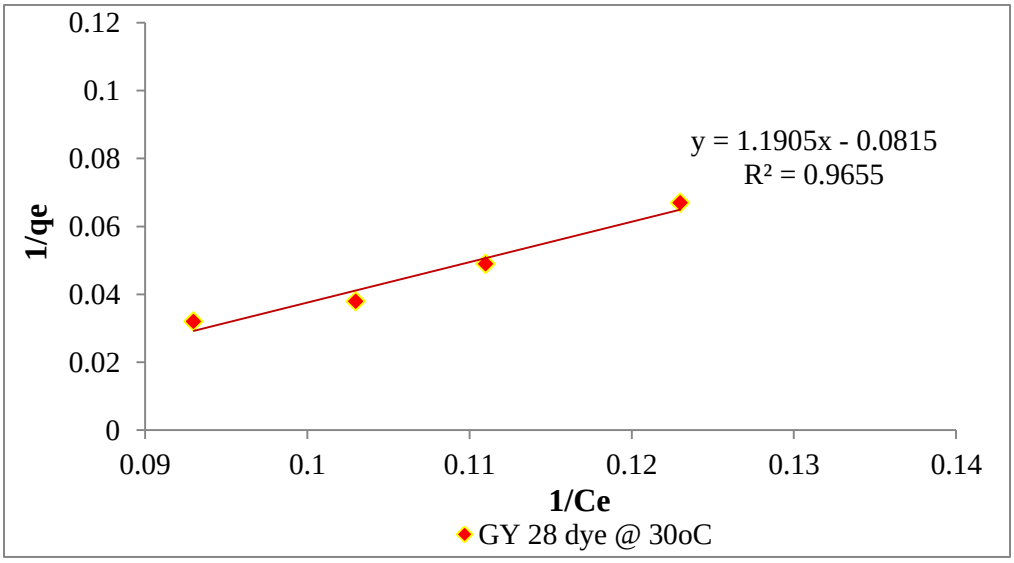
Monolayer adsorption can be often described by Langmuir equation. The model assumes that the adsorption is a process which occurs in a uniform energy of adsorption, homogeneous surface, in which the molecules form a monolayer of adsorbate on the surface of the material, each active site adsorbs one molecule only and preventing the transmigration means no interaction among the adsorbed molecules at a constant temperature. The Langmuir isotherm model can be represented by equation 4.2

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{qmKL}\left[\frac{1}{Ce}\right] \qquad (4.2)$$

The values $q_m$ and $K_L$ were computed from the intercept and slope of the Langmuir plot of 1/qe versus 1/Ce, respectively.

According to the results presented below in Figure 4.15 and Table 4.11, the result shows good correlation with the Langmuir isotherm model based on by the $R^2$ values 0.9655 and 0.9861 for GY 28 dye which is close to unity at 30$^o$C and 40$^o$C respectivily. This result works for GY 28 dyes meaning that the overall process can be modelled as monolayer coverage of dye molecules on the surface of the BM5 activated carbon. From Table 4.11 the value of $K_L$ (L $mg^{-1}$ ) is the Langmuir constant related to the affinity of the binding sites and energy of adsorption: the higher the $K_L$ value, the higher the affinity of the binding sites.

The separation/ factor ($R_L$) is an important parameter of the Langmuir isotherm that can be used to verify if the adsorption in the system is favorable ($0 < R_L < 1$). For the value of concentrations studied 50 mg $L^{-1}$ at 30$^o$C and 40$^o$C, the $R_L$ values 0.23 and 0.24 using equation 2.5, indicating that the system is favorable means it showing that the adsorption of GY 28 dye on BM5 was best.



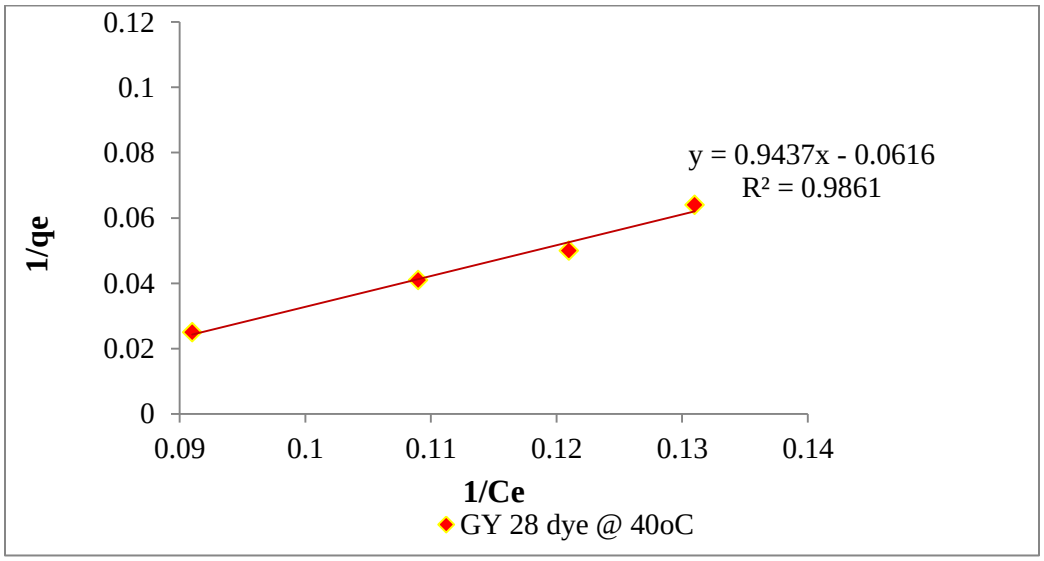



Figure 4.15 Langmuir isotherm model for GY 28 dye (a) at 30 $^{o}$C and (b) at 40 $^{o}$C

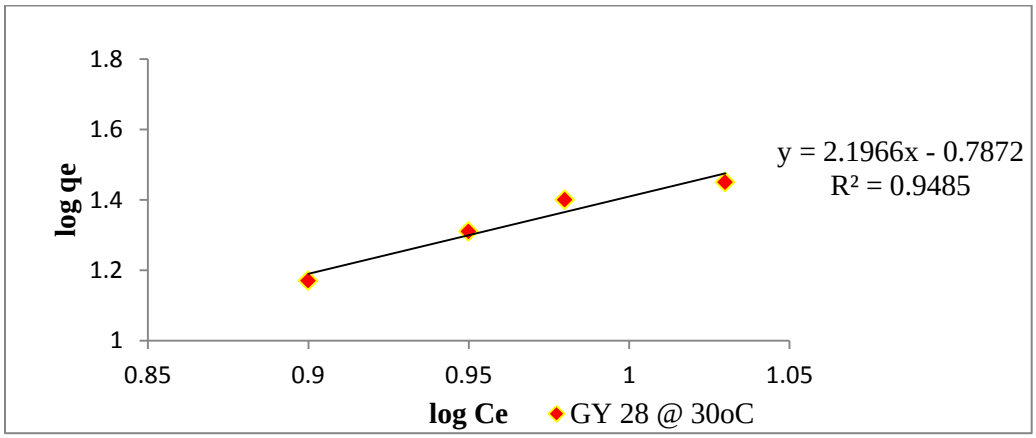
### 4.6.2 Freundich isotherm model

The Freundlich isotherm is well-know isotherm which gives basic description of the adsorption of liquid molecules on solid surfaces. Freundlich model is based on sorption on a heterogeneous surface of varied affinitie. The Freundlich equa- tion is used to describe heterogeneous systems and reversible ad- sorption and is not restricted to the formation of monolayers. The linearized form of Freundlich model is expressed as the follows equation:

$$\log[qe] = \log[Kf] + \frac{1}{n}\log[Ce] \qquad (4.3)$$

Where: $K_f$ is the Freundlich constant related to the adsorption capacity and 1/n is an indicator of adsorption intensity. Value for 1/n below 1 indicates a normal and favolurable adsorption and the surface is more heterogeneous with more functional groups which favours the adsorption and also high value of kf shows easy uptake of the dye (Srinivasan *et al.*, 2013).

The Freundlich isotherm model constants, n and $K_f$, were computed from the slope and intercept of the equation for the graph (log qe) vs (log Ce), respectively. The fit of the data to the Freun- dlich isotherm was also tested by the slope 1/n and $R^2$ values of the plot, which gave good result; it's presented in Table 4.11.



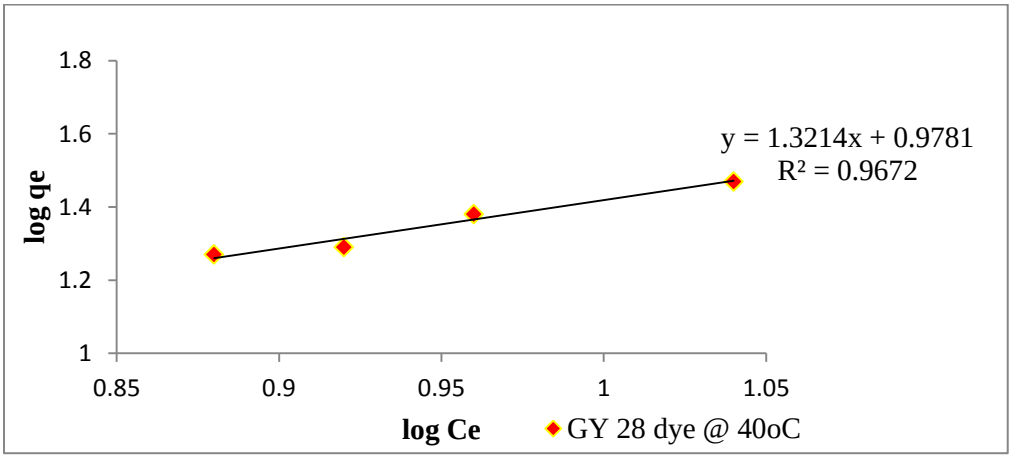




Figure 4.16 Freundlich isotherm model for GY 28 dye

Table 4.11 Langmuir and Freundlich isotherm constants for GY 28 dye

| Adsorption Isotherm | Isotherm Parameters | Tempereture, $^{o}$C | |
|---|---|---|---|
| | | 30 $^{o}$C | 40 $^{o}$C |
| Langmuir $\frac{1}{qe} = \frac{1}{qm} + \frac{1}{qmKL}(\frac{1}{Ce}$ | $q_m$ (mg/g) | 12.27 | 16.23 |
| | $K_L$ (L/mg) | 0.068 | 0.065 |
| | $R_L$ | 0.23 | 0.24 |
| | $R^2$ | 0.9655 | 0.9861 |
| Freundlich $\log(qe) = \log(Kf) + \frac{1}{n}\log(Ce)$ | $K_f$ (mg/g) | 6.13 | 9.51 |
| | 1/n | 2.1966 | 1.3214 |
| | $R^2$ | 0.9485 | 0.9672 |

The adsorption isotherm of GY 28 dye adsorption onto BM5 was showed in Figure 4.15 and 4.16. Langmuir and Freundlich isotherms were widely used in describing adsorption organic pollutants onto porous materials. In current study, Freundlich isotherm was selected in fitting adsorption data during the experimental period. According to experiences of previous studies on adsorption of pollutants onto the surface of BM5, the Langmuir isotherm model was selected to explain how adsorption takes place for GY 28 dye onto BM5. In Langmuir fitting see Figure 4.15, results of high degree of linear fitting between 1/qe vs. 1/Ce were obtained ($R^2$ = 0.9655 and $R^2$= 0.9861) at a 30 and 40$^o$C. The fitting of the model was highly significant as it suggests the monolayer coverage of the GY 28 dye on the surface of the BM5. But in this study we observed the effect of temperature on the adsorption capacity on the surface of modified activated carbon. So based on Table 4.11 that the Langmuir and Freundlich isotherm constants values for GY 28 dye on surface of BM5 indicated that increased of temperature which favorable for adsorption processes.

### 4.7 Adsorption Kinetics analysis

Adsorption kinetics models are used in order to explain the adsorption mechanism and characteristics of adsorption. So, in order to evaluate the performance of the adsorbent for GY 28 dye removal and to predict the residence time needed for an adsorption study, two common well know kinetic models were used to describe the experimental data: pseudo first order and pseudo second order. Determination of best fit kinetic model is the most common way to predict the optimum adsorption kinetic expression. In this study, adsorption kinetics of GY 28 dye has been carried out to understand the adsorption behavior of BM5 activated carbon with respect to contact time. The initial dye concentration used are 50 ppm and 150 ppm by controlling the adsorption capacity of GY 28 dyes.

#### 4.7.1 Pseudo first-order kinetics model

Pseudo first-order kinetics model is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase. A linear form of the pseudo first order kinetic model known as Lagergren rate equation expressed as follows (Aktaş & Ferhan, 2012):

$$\log\ (qe - qt) = \log(qe)\ - (\frac{k1t}{2.303}) \quad (4.4)$$

Where: qe and qt (mg/gm) = Adsorption capacity at equilibrium and at time t, respectively

$K_1$ ($min^{-1}$) = Rate constant of pseudo first-order kinetics

The plot of log (qe – qt) versus t should give a linear relationship from which $K_1$ and qe can be determined from the slop and intercept of the plot, respectively from figure 4.17.

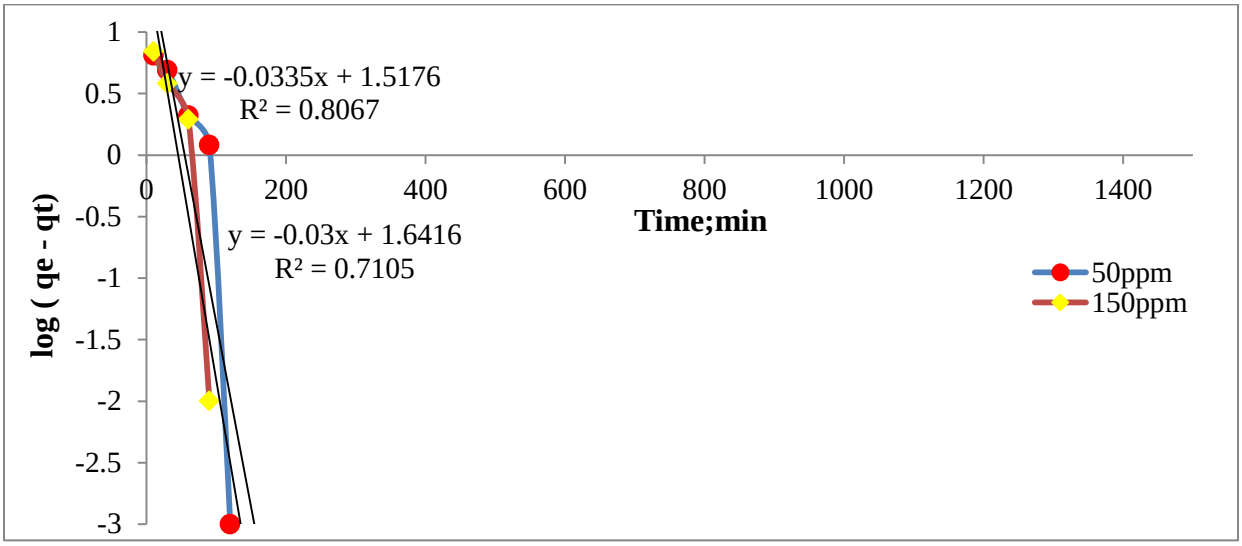



Figure 4.17 Pseudo 1st order kinetic for GY 28 dye

### 4.7.2 Pseudo second-order kinetics model

The adsorption kinetics was also described as pseudo-second order kinetics using equation; (Ghaedi *et al.*, 2012)

$$\frac{t}{qt} = \frac{1}{k2qe2} + \left(\frac{1}{qe}\right)t \qquad (4.5)$$

Where: qe and qt = adsorption capacities at equilibrium and at time t, respectively (mg/g)

$K_2$ = rate constant of pseudo-second-order sorption (g/mg.min)

The constants qe and $K_2$ were computed from the slop and intercept of t/qt versus t linear plot, respectively from figure 4.18.

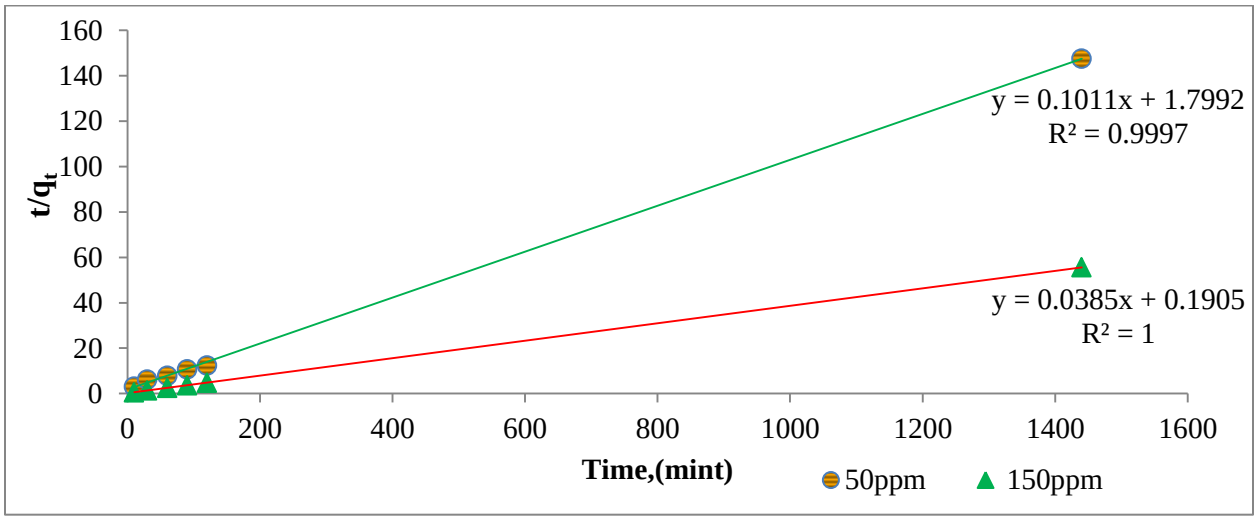



Figure 4.18 Pseudo 2nd order kinetic for GY 28 dye

Table 4.12 The Pseudo first and second-order constants for GY 28 dye

| $C_o$, ppm | $q_e$, exp (mg/g) | Pseudo 1st order kinetics | | | Pseudo 2nd order kinetics | | |
|---|---|---|---|---|---|---|---|
| | | $q_e$,cal (mg/gm) | $K_1$ (g/mg.min) | $R^2$ | $q_e$, cal (mg/g) | $K_2$ (g/mg.min) | $R^2$ |
| 50 | 9.72 | 0.51 | 3.78 | 0.7105 | 9.89 | 0.0057 | 0.9997 |
| 150 | 25.16 | 0.46 | 3.49 | 0.8067 | 25.97 | 0.0078 | 1 |

From above figures 4.17 and 4.18, the two kinetic models were selected to study the adsorption kinetic of GY 28 dye onto the surface of BM5. Obviously, Pseudo-second order model see Figure 4.17 could fit the experimental results better than pseudo-first order model. From Table 4.12 showed the kinetic parameters for different initial concentrations of GY 28 dye obtained utilizing two adsorption kinetic models. The pseudo-second order model generated a high degree of fitting ($R^2$= 0.9997 and $R^2$ =1). The rate constants, $k_2$ for pseudo-second order decreased with the increase of initial concentration of GY 28 dye (50 –150 ppm). This phenomenon is probably due to the lower competition for the adsorption sites at lower initial concentration of GY 28. Similarly, the competition for the surface active sites will be stronger at higher initial concentration and the adsorption rates were consequently decreased. The pseudo-second order model is based on the assumption that the rate-limiting factor in the adsorption was determined by chemisorption. Thus, the GY 28 adsorption process onto modified peanut shell was a chemisorption rather than physical sorption.

# 5. CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

The study results presented indicate that the agro by-product like peanut shells provide a suitable option for the preparation of activated carbon with chemical (NaOH) activation in terms of the adsorption removal efficiency and capacity towards the basic dye like GY 28 dye from aqueous solution. The adsorption efficiency tests were performed in the batch adsorption system at different initial concentrations of adsorbate (GY 28: 30-150 ppm), contact time (10-90 mint), and solution pH (2-10) with 100 ml volume of solution at constant solution temperature (25 $\pm$ 5°C) and 150 rpm. In this study, the adsorption efficiency of BM5 and Bi-Ch5 were investigated in detail by considering various factors that affect the adsorption process such as pH, initial dye concentration and time by starting from the proximate analysis of the BM5. The adsorption process was strongly pH dependent since the higher removal percentage of 86.7% was obtained at a pH value of 10. The effect of contact time shows a rapid adsorption of dye in the first 10 min and thereafter, the adsorption rate slowly increases to reach equilibrium in about 60 min. While a time of 2hrs was obtained as optimum for the adsorption process after test for used concentrations. Therefore, the prepared activated carbon (BM5) has shown to be an effective adsorbent for the removal of GY 28 dye from aqueous solution. The values obtained are an agreement with that of design expert 6.0.8 software and the result shows the model and interaction effects are significant.

Adsorption efficiency, surface characteristics and yield of modified activated carbon was depended on the effect of activation agent and carbonization temperature. In all cases, increasing the carbonization temperatures from 400 to 600°C with activation time of 180 min showed a decrease in the percentage yield while the adsorption removal efficiency and capacities were increased with specified parameters. Based on the physicochemical properties of the RPS and sodium hydroxide modified PS based carbon (BM5) like BET surface area, FT-IR, XRD, $pH_{PZC}$ and proximate analysis; BM5 prepared activated carbons possess high specific surface areas with more remove of GY 28 dye from aqueous solution while FTIR analyses verified the presence of various functional groups on the surface of activated carbons. So, FTIR analysis showed that the presence of hydroxyl, carbonyl, aliphatic, ethers, alcohol, phenol and carboxylic functional groups on the surfaces of the raw material and BM5 activated carbon with some modification. The XRD result reveals that raw PS and BM5 produced activated carbons were found to be crys-

talline. The crystallized structure of BM5 was stable after the adsorption by comparing XRD patterns for original and GY 28 dye loaded BM5.

The adsorption isotherm and kinetic study were also carried out in order to understand the mechanism of the adsorption process. The experimental data were fitted with the equations of Langmuir and Freundlich isotherm model. The result indicated that the adsorption process followed both models for a given temperature. The adsorption kinetics was also investigated to determine the rate of adsorption using pseudo first and second order kinetics models. The Pseudo-second order kinetic almost perfectly than the Pseudo first order kinetics based on given data.

Generally, In this work the modified activated carbons demonstrate the effectiveness for the removal of GY 28 dye from aqueous solution.

## 5.2 Recommendation

In this paper work is mainly foucs on the study of the effect of activation agent and carbonization temperature on the adsorption efficiency, surface characteristics and yield of prepared activated carbon for use on the treatment of aqueous basic daye solution. BM5 AC has a promising potential for the removal of GY 28 of dyes from aqueous solution and real wastewater based on physical observation. But as most wastewater from industry contain a lot of different pollutants than just water and dyes, there is a need to undertake further research on the material. The most important further research works are identified below.

- Characterization of the RPS and BM5 using advanced techniques such as SEM; to determine the surface morphology of the adsorbent, and TGA (Thermogravimetric analysis); to analysis the pyrolysis behaviors of the material.
- How to manage the hot discharge gases (smoke), nitrogen gas and the volatile matter passing out from the reactor and also water after washing the prepared activeted carbon which conatines some unwanted chemicals.
- Details compare the performance of activated carbon produced in the laboratory with the imported commercial activated carbon on aqueous solution and real wastewater.
- The efficiency of this material should also be investigated for the removal of heavy metals, BOD and COD from aqueous solution and also on the real wastewater containing all sorts of pollutants.
- The regeneration potential of the used BM5 should be studied before the commercial application of the material means desorption of BM5 studies was carried in order to examine further into the mechanistic aspects of the GY 28 dye adsorption onto prepared AC.
- Finally, column performance of BM5 should be investigated and the possibility of designing a fixed packed bed adsorber that removes significant amount of pollutants including COD, BOD, heavy metal, and dye pollutants.

## REFERENCE

Abbas, A., Murtaza, S., Shahid, K., Munir, M., Ayub, R., & Akber, S. (2012). Comparative Study of Adsorptive Removal of Congo Red and Brilliant Green Dyes from Water Using Peanut Shell. *Middle-East Journal of Scientific Research*, *11*(6), 828–832.

Adegoke, K. A., & Solomon, O. (2015). Dye sequestration using agricultural wastes as adsorbents. *Water Resources and Industry*, *12*, 8–24.

Adib, M., Al-qodah, Z., & Ngah, C. W. Z. (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production : A review. *Renewable and Sustainable Energy Reviews*, *46*, 218–235.

Adil Jaafar and Abdelghani Boussaoud,(2014). Disappearance of Basic yellow 28 from aqueous solution by Fenton's reagent. Journal of Master Environmental of Science, 5 (2), 2426-2431.

Aiyer, S. S. C. ., Ramachandran, S. ., Thiruma Valavan, K. ., & Prakash Kumar, B. G. (2015). A review of solar photocatalytic degradation of wastewater using advanced oxidation processes. *Journal of Industrial Pollution Control*, *31*(2), 297–309.

Aksu, Z. (2005). Application of biosorption for the removal of organic pollutants : a review. *Process Biochemistry*, *40*, 997–1026.

Aktaş, Ö., & Ferhan, Ç. (2012). Fundamentals of Adsorption onto Activated Carbon in Water and Wastewater Treatment. *Activated Carbon for wastewater Treatment: Integration of Adsorption and Biological Treatment*. 13-42

Ali, R., & Naushad, M. (2012). Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell : Adsorption kinetics , equilibrium and thermodynamic studies. *Chemical Engineering Journal*, *184*, 238–247.

Aljeboree, A. M., Alshirifi, A. N., & Alkaim, A. F. (2014). Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. *Arabian Journal of Chemistry*,

Anastopoulos, I., & Kyzas, G. Z. (2014). Agricultural peels for dye adsorption : A review of recent literature. *Journal of Molecular Liquids*.

Apaydın-varol, E., & Pütün, E. (2012). Journal of Analytical and Applied Pyrolysis Preparation and characterization of pyrolytic chars from different biomass samples, *98*, 29–36.

Aworn, A., Thiravetyan, P., & Nakbanpote, W. (2008). Preparation and characteristics of agricultural waste activated carbon by physical activation having micro- and mesopores. *Journal of Analytical and Applied Pyrolysis*,*82*, 279–285.

Azeb G.M, Beteley T. (2016). Study of adsorption performance of bagasse fly ash for removal of malachite green and methylene blue dye mixture from aqueous solution, *School of Chemical and Bio Engineering*, AAiT.

Banerjee, S., & Sharma, Y. C. (2013). Equilibrium and kinetic studies for removal of malachite green from aqueous solution by a low cost activated carbon. *Journal of Industrial and Engineering Chemistry*, *19*(4), 1099–1105.

H. D Beyene. (2014). The potential of dyes removal from textile wastewater by using different treatment technology , a Review. *International Journal of Environmental Monitoring and Analysis* , *2*(6), 347–353.

Bhatnagar, A., & Sillanpää, M. (2010). Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment ;A review. *Chemical Engineering Journal*, *157*, 277–296.

Borah, L., Goswami, M., & Phukan, P. (2015). Adsorption of methylene blue and eosin yellow using porous carbon prepared from tea waste : Adsorption equilibrium , kinetics and thermodynamics study. *Journal of Environmental Chemical Engineering*, *3*(2), 1018–1028.

Chen, L., Wang, X., Yang, H., Lu, Q., Li, D., Yang, Q., & Chen, H. (2015). Study on pyrolysis behaviors of non-woody lignins with TG-FTIR and Py-GC/MS. *Journal of Analytical and Applied Pyrolysis* ,1-9

M. E. Ossman, M. S. Mansour, M. A. Fattah1*, N. Taha, Y. Kiros. (2014). Peanut shells and talc powder for removal of hexavalent chromium from aqueous solutions. *Bulgarian Chemical Communications*, 46(3) , 629 – 639.

Costa, C., Ma, M. C., & Barraga, B. E. (2007). Biodegradation of azo dyes by bacteria

inoculated on solid media. *Dyes and Pigments*, *75*, 73–81.

Dabrowski,V.A.Tertykh. (1996). Adsorption on new and modified inorganic sorbents. Journal of Elsevier studies in surface science and catalysis.

Dawood, S., & Sen, T. K. (2014). Review on Dye Removal from Its Aqueous Solution into Alternative Cost Effective and Non-Conventional Adsorbents. *Journal of Chemical and Process Engineering,1(104)*. 1-11

Demirbas, A. (2009). Agricultural based activated carbons for the removal of dyes from aqueous solutions : A review. *Journal of Hazardous Materials journal*, *167*, 1–9.

Dias, J. M., Alvim-ferraz, M. C. M., Almeida, M. F., & Sa, M. (2007). Waste materials for activated carbon preparation and its use in aqueous-phase treatment : A review. *Journal of Environmental Management* , *85*, 833–846.

Djilani, C., Zaghdoudi, R., Djazi, F., & Bouchekima, B. (2015). Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon. *Journal of the Taiwan Institute of Chemical Engineers*, *0*, 1–10.

Eren, E., & Afsin, B. (2008). Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated bentonite surfaces. *Dyes and Pigments*, *76*, 220–225.

Ezechi, E. H., Kutty, S. R. B. M., Malakahmad, A., & Isa, M. H. (2015). Characterization and optimization of effluent dye removal using a new low cost adsorbent: Equilibrium, kinetics and thermodynamic study. *Process Safety and Environmental Protection*, *98*, 16–32.

Ferreira, A. M., Coutinho, J. A. P., Fernandes, A. M., & Freire, M. G. (2014). Complete removal of textile dyes from aqueous media using ionic-liquid-based aqueous two-phase systems. *Separation and purification technology*, *128*, 58–66.

Filipkowska, U., Zadrożna, M. K., Jóźwiak, T., Szymczyk, P., & Kaczyński, A. (2015). A dsorption of basic yellow 28 ( BY 28 ) and acid yellow 23 ( AY 23 ) dyes onto chitin, *Progress on Chemistry and Application of Chitin and its Derivatives*, 34–42.

Georgin, J., Dotto, G. L., Mazutti, M. A., & Foletto, E. L. (2016). Preparation of activated

carbon from peanut shell by conventional pyrolysis and microwave irradiation-pyrolysis to remove organic dyes from aqueous solutions. *Journal of Environmental Chemical Engineering*, *4*(1), 266–275.

Ghaedi, M., Sadeghian, B., Pebdani, A. A., Sahraei, R., Daneshfar, A., & Duran, C. (2012). Kinetics , thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon. *Chemical Engineering Journal*, *187*, 133–141.

Ghoreishi, S. M., & Haghighi, R.(2003). Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent. *Chemical Engineering Journal*,*95*, 163–169.

Gong, R., Sun, Y., Chen, J., Liu, H., & Yang, C. (2005). Effect of chemical modification on dye adsorption capacity of peanut hull. *Dyes and Pigments*, *67*(3), 175–181.

Gopal, N., Asaithambi, M., Sivakumar, P., & Sivakumar, V. (2014). Adsorption studies of a direct dye using polyaniline coated activated carbon prepared from Prosopis juliflora. *Journal of Water Process Engineering*, *2*, 87–95.

Grace, B. L., College, G. J., Sivamani, S., (2009). Removal of Dyes from Wastewater using Adsorption - A Review. Journal of *Biosorption of Dyes* , 2(4), 47-51.

Guo, J., Li, B., Liu, L., & Lv, K. (2014). Removal of methylene blue from aqueous solutions by chemically modified bamboo. *Chemosphere*, *111*, 225–231.

Gupta, A., & Balomajumder, C. (2015). Simultaneous adsorption of Cr ( VI ) and phenol onto tea waste biomass from binary mixture : Multicomponent adsorption , thermodynamic and kinetic study. *Journal of Environmental Chemical Engineering*, *3*(2), 785–796.

Gupta, V. K. (2009). Application of low-cost adsorbents for dye removal -A review. *Journal of Environmental Management*, *90*(8), 2313–2342.

Gupta, V. K., Kumar, R., Nayak, A., Saleh, T. A., & Barakart, M. A. (2013). Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: A review. *Advances in Colloid and Interface Science*, 1-54.

Hameed, B. H., & Rahman, A. A. (2008). Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material. *Journal of Hazardous Materials,160*, 576–581.

Hassan, A. F., & Youssef, A. M. (2014). Preparation and characterization of microporous NaOH- activated carbons from hydrofluoric acid leached rice husk and its application for lead ( II ) adsorption. *Korean Carbon Society under carbon etters,15*(1), 57–66.

Holkar, C. R., Jadhav, A. J., Pinjari, D. V, Mahamuni, N. M., & Pandit, A. B. (2016). A critical review on textile wastewater treatments : Possible approaches. *Journal of Environmental Management*, *182*, 351–366.

Honoré P., Ouattara K., Irié M., Bi G., Kouakou U., Dembele A., Trokourey A. (2014). Preparation and Characterization of Activated Carbons Based On Peanut Shell ( Arachis Hypogaea ) Green Soya Shell ( Vigna Radiata ). *International Journal of Science and Research,3(7),* 933–937.

F. Rodriguez-Reinoso And M. Molina-Sabio (1992). Activated carbons from lignocellulosic materials by chemical and / or physical activation : an overview. Carbon. 30(7), 1111-1118.

Iqbal, M. J., & Ashiq, M. N. (2007). Adsorption of dyes from aqueous solutions on activated charcoal. *Journal of Hazardous Materials,139*, 57- 66.

Joseph, N. T., Chinonye, O. E., Philomena, I. K., Christian, A. C., & Elijah, O. C. (2016). Isotherm and kinetic modeling of adsorption of dyestuffs onto kola nut (Cola acuminata) shell activated carbon. *Journal of Chemical Technology and Metallurgy*, *51*(2), 188–201.

M. Saban Tanyildizi. (2011). Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull. *Chemical Engineering Journal ,168*, 1234–1240.

Kandasamy, J., Vigneswaran, S., Hoang, T. T. L., & Chaudhary, D. N. S. (2006). Adsorption and biological filtration in wastewater treatment. *Encyclopedia of Life Support System*.1 -14.

Kharub, M. (2012). Use of various technologies , methods and adsorbents for the removal of dye. *Journal of Environmental Research And Development , 6*(3), 879-883.

Köneço, G., Toygun, Ş., Kalpakl, Y., & Akgün, M. (2015). Photocatalytic degradation of textile dye CI Basic Yellow 28 wastewater by Degussa $P_2S$ based $TiO_2$. *Advances in Environmental Research ,4(1),* 25–38.

Koumanova, B., Allen, S. J., & Koumanova, B. (2005). Decolourisation of water / wastewater using adsorption - A review. *Journal of the University of Chemical Technology and Metallurgy, 40(3),* 175–192.

Kulkarni, M. R., Revanth, T., Acharya, A., & Bhat, P. (2017). Removal of Crystal Violet dye from aqueous solution using water hyacinth : Equilibrium , kinetics and thermodynamics study. *Resource-Efficient Technologies*. 1-7.

Shrestha Rajeshwar M, Yadav Amar P, Pokharel Bhadra P and Pradhananga Raja Ram. (2012). Preparation and Characterization of Activated Carbon from Lapsi ( Choerospondias axillaris ) Seed Stone by Chemical Activation with Phosphoric acid. *Research Journal of Chemical Sciences*, *2*(10), 80–86.

Mahmoudi, K., Hamdi, N., & Srasra, E. (2014). Preparation and characterization of activated carbon from date pits by chemical activation with zinc chloride for methyl orange adsorption, *5*(6), 1758–1769.

Malik, R., Ramteke, D. S., & Wate, S. R. (2006). Physico-chemical and surface characterization of adsorbent prepared from groundnut shell by $ZnCl_2$ activation and its ability to adsorb colour. *Indian Journal of Chemical Technology*, *13*(4), 319–328.

Mane, V. S., & Babu, P. V. V. (2011). Studies on the adsorption of Brilliant Green dye from aqueous solution onto low-cost NaOH treated saw dust. *Desalination*, *273*(3), 321–329.

Manoj, P., Reddy, K., Verma, P., & Subrahmanyam, C. (2015). Bio-waste derived adsorbent material for methylene blue adsorption. *Journal of the Taiwan Institute of Chemical Engineers*, *0*, 1–9.

Gregorio Crini. (2006). Non-conventional low-cost adsorbents for dye removal - A review. *Bioresource Technology*, *97*, 1061–1085.

Paraskeva P., Kalderis D., & Diamadopoulos E.(2008). Production of activated carbon from

agricultural byproducts. *Journal of Chemical Technology and Biotechnology*,*83*(5),581–592.

Postai D. L., Demarchi C. A., Zanatta F., Rodrigues A., Caroline D., & Melo C. (2016). Adsorption of rhodamine B and methylene blue dyes using waste of seeds of Aleurites Moluccana , a low cost adsorbent. *Alexandria Engineering Journal , 55*, 1713–1723.

B.O. Ogunsile, I.F.Odesola, O. Oluwole and A.H. Labulo . (2014). Production and Characterization of Activated Carbon from Chemically Treated Agricultural Wastes. Journal of Applied Sciences Research, 10(12), 29-35.

Rafatullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of methylene blue on low-cost adsorbents : A review. *Journal of Hazardous Materials*, *177*(3), 70–80.

Sabrin A, A. A. (2015). Textile Dye Removal from Wastewater Effluents Using Chitosan-ZnO Nanocomposite. *Journal of Textile Science & Engineering*, *5*(3), 5–8.

Sadaf, S., & Bhatti, H. N. (2014). Batch and fixed bed column studies for the removal of Indosol Yellow BG dye by peanut husk. *Journal of the Taiwan Institute of Chemical Engineers*, *45*(2), 541–553.

Şahin, Ö., Saka, C., Ceyhan, A. A., & Baytar, O. (2016). Environmental Effects The pyrolysis process of biomass by two-stage chemical activation with different methodology and iodine adsorption. *Journal of Energy Sources, Part A: Recovery, Utilization, And Environmental Effects* ,38(12), 1756-1762.

Salleh, M. A. M., Mahmoud, D. K., Karim, W. A. W. A., & Idris, A. (2011). Cationic and anionic dye adsorption by agricultural solid wastes - A comprehensive review. *Desalination*, *280*(3), 1–13.

Santos, B., Cervantes, F. J., & Lier, J. B. Van. (2007). Review paper on current technologies for decolourisation of textile wastewaters : Perspectives for anaerobic biotechnology. *Bioresource Technology , 98*, 2369–2385.

Seey, T. A., Jain, M., & Mohd, N. (2012). Characterization of mangrove bark adsorbent and its application in the removal of textile dyes from aqueous solutions. *Journal of Applied Phytotechnology in Environmental Sanitation*, *1*(3), 121–130.

Sharma, S., Saxena, R., & Gaur, G. (2014). Study of Removal Techniques for Azo Dyes by Biosorption - A Review. *Journal of Applied Chemistry, 7(10)*, 6–21.

Song, J., Zou, W., Bian, Y., Su, F., & Han, R. (2011). Adsorption characteristics of methylene blue by peanut husk in batch and column modes. *Desalination*, *265*(3), 119–125.

Srinivasakannan, C., Zailani, M., & Bakar, A. (2004). Production of activated carbon from rubber wood sawdust. *Biomass and Bioenergy*, *27*, 89–96.

Srinivasan, P., Sivakumar, P., & Raja, S. (2013). Kinetic and isotherm studies for the adsorption of a textile dye using PVA matrix supported activated carbon. *Archives of Applied Science Research*, *5*(6), 132–140.

Sulyman, M., Namiesnik, J., & Gierak, A. (2017). Low-cost Adsorbents Derived from Agricultural By-products / Wastes for Enhancing Contaminant Uptakes from Wastewater - A Review. *Journal of Environmental Studies*, *26*(2), 479–510.

Syafalni, S. (2012). Treatment of Dye Wastewater Using Granular Activated Carbon and Zeolite Filter. *Modern Applied Science*, *6*(2), 37–51.

Taşar, Ş., Kaya, F., & Özer, A. (2014). Biosorption of lead(II) ions from aqueous solution by peanut shells: Equilibrium, thermodynamic and kinetic studies. *Journal of Environmental Chemical Engineering*, *2*(2), 1018–1026.

Taylor, P., Boudrahem, F., & Soualah, A. (2015). Removal of basic yellow dye from aqueous solutions by sorption onto reed as an adsorbent. Desalination and Water Treatment, 54(6), 1727-1734

Terrones, M., & Terrones, M. (2015). Production of activated carbon from agricultural raw waste. *IOSR Journal of Engineering* , *5*(5), 54-63.

Tunali, S., Özcan, A. S., Akar, T., Özcan, A., & Kaynak, Z. (2009). Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste. *Desalination*, *249*(2), 757–761.

Wang, X., Chen, H., Yang, H., Wang, J., & Xin, F. (2011). The influence of alkali and alkaline earth metal compounds on pyrolysis of peanut shell. *Asia-Pacific Journal Of Chemical*

*Engineering*, 1-6.

Wang, Z., Xue, M., Huang, K., & Liu, Z. (2010). Textile Dyeing Wastewater Treatment. *Advances in Treating Textile Effluent*, 91-116.

Wilson, K., Yang, H., Seo, C. W., & Marshall, W. E. (2006). Select metal adsorption by activated carbon made from peanut shells. *Bioresource Technology*, *97*, 2266–2270.

Witek-Krowiak, A., Szafran, R. G., & Modelski, S. (2011). Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent. *Desalination*, *265*(3), 126–134.

Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption : A review. *Advances in Colloid and Interface Science*. *209*, 172–184.

Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption : A review. *Advances in Colloid and Interface Science*, *209*, 172–184.

Yang, H. (2007). Characteristics of hemicellulose , cellulose and lignin pyrolysis. *Fuel*, *86*, 1781–1788.

Yener, J., Kopac, T., Dogu, G., & Dogu, T. (2008). Dynamic analysis of sorption of Methylene Blue dye on granular and powdered activated carbon. *Chemical Engineering Journal*, *144*, 400–406.

Zhao, B., Xiao, W., Shang, Y., Zhu, H., & Han, R. (2014). Adsorption of light green anionic dye using cationic surfactant-modified peanut husk in batch mode. *Arabian Journal of Chemistry*. 1-8.

# APPENDICES

## Appendix A: BET analysis for BM5 AC

Quantachrome QuadraWin - Data Acquisition and Reduction
for QuadraSorb SI

version 5.04

| | | | | | |
|---|---|---|---|---|---|
| Analysis Operator: | operator | Date:12/14/2017 | Report Operator: operator | | Date:2017/12/14 |
| Sample ID: | BM_5 | Filename: | BM_5.QPS | | |
| Sample Desc: | | Comment: | | | |
| Sample weight: | 0.3528 g | | | | |
| Analysis Time: | 854.9 min | End of run: | 12/14/2017 0:38:42 | Instrument: | QuadraSorb Station 2 |
| Void Vol.: | He Mode.Cell: 9mm large bulb | Run mode | Standard | Instrument version: | 5.04 |
| Outgas Time: | 24.0 hrs | OutgasTemp: | 200.0 C | | |
| Analysis gas: | Nitrogen | Bath Temp: | 77.3 K | | |

Press. Tolerance:0.050/0.050 (ads/des) Equil time: 200/200 sec (ads/des) Equil timeout:400/400 sec (ads/des)

Data Reduction Parameters

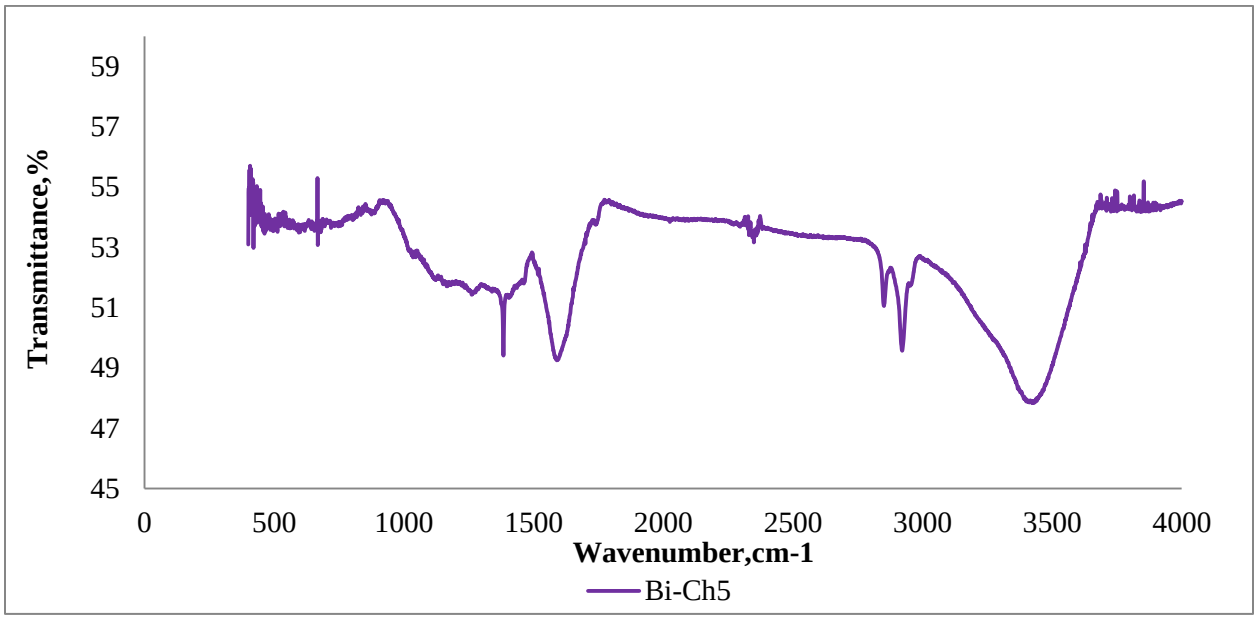
| | | | | | |
|---|---|---|---|---|---|
| Adsorbate | Nitrogen | Temperature | 77.350K | | |
| Molec. Wt.: | 28.013 | Cross Section: | 16.200 Å² | Liquid Density: | 0.808 g/cc |

| Relative Pressure P/Po | Volume @ STP cc/g | 1 / [ W((Po/P) - 1) ] |
|---|---|---|
| 4.96172e-02 | 40.2774 | 1.0371e+00 |
| 9.16458e-02 | 46.4272 | 1.7387e+00 |
| 1.34782e-01 | 48.5096 | 2.5694e+00 |
| 1.79915e-01 | 52.1883 | 3.3634e+00 |
| 2.25918e-01 | 55.1550 | 4.2338e+00 |
| 2.71434e-01 | 56.9250 | 5.2365e+00 |
| 3.14209e-01 | 57.7655 | 6.3461e+00 |

BET summary

| | |
|---|---|
| Slope = | 19.761 |
| Intercept = | -7.462e-02 |
| Correlation coefficient, r = | 0.997619 |
| C constant= | -263.810 |
| Surface Area = | 973.600 m²/g |

## Appendix B: FT-IR analysis of Bi-Ch5 AC



## Appendix C: Fourier Transform Infrared Spectroscopy (FTIR) correlation table

| Functional Group Names | Absorption Ranges($cm^{-1}$) | Type of Vibration causing IR absorption |
|---|---|---|
| Alkanes | 3000-2800 | H-C-H asymmetric & symmetric stretch |
| | 1500-1440 | H-C-H bend |
| Alkenes | 3100-3000 | C=C-H asymmetric stretch |
| | 1675-1600 | C-C=C symmetric stretch |
| Alkynes | 3300-3200 | C-H stretch |
| | 2200-2100 | C-C stretch |
| Aromatic Rings | 3100-3000 | C=C-H asymmetric Stretch |
| | 1600-1580 | C-C=C symmetric stretch |
| | 1500-1450 | C-C=C asymmetric stretch |
| Phenols & alcohols | 3600-3100 | Hydrogen-bonded O-H stretch |
| Carboxylic Acids | 3400-2400 | Hydrogen-bonded O-H stretch |
| | 1730-1650 | C=O stretch |
| Ketones | 1750-1625 | C=O stretch |
| Aldehydes | 1750-1625 | C=O stretch |
| | 2850-2800 | C-H stretch off C=O |
| | 2750-2700 | C-H stretch off C=O |
| Esters | 1755-1650 | C=O stretch |
| | 1300-1000 | C-O stretch |
| Amines-Primary | 3500-3100 | N-H stretch |
| | 1640-1560 | N-H bend |
| Amines-Secondary | 3500-3100 | N-H stretch |
| Nitriles | 2300-2200 | C-N stretch |
| Nitro Groups | 1600-1500 | N=O stretch |
| | 1400-1300 | N=O bend |
| Amides | 3500-3100 | N-H stretch |
| | 1670-1600 | C=O stretch |
| | 1640-1550 | N-H bend |

## Appendix D: Adsorption Data using for Design Expert software 6.0.8

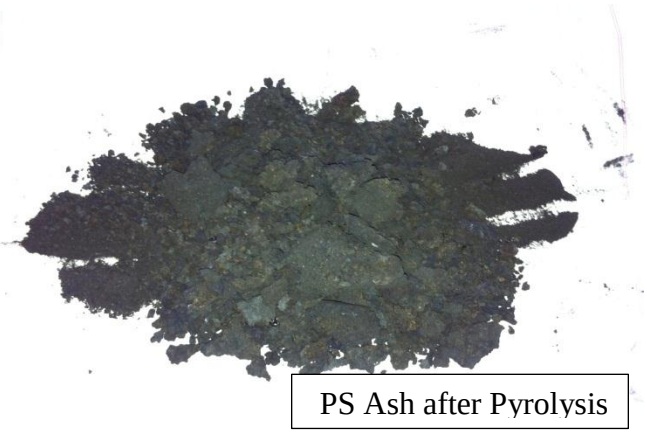
| Std | Run | Block | Factor 1 A:pH | Factor 2 B:concentration;ppm | Factor 3 C:contact time; mint | Response 1 % Removal |
|---|---|---|---|---|---|---|
| 1 | 24 | Block 1 | 3.00 | 50.00 | 30.00 | 50.2 |
| 2 | 17 | Block 1 | 6.50 | 50.00 | 30.00 | 60.3 |
| 3 | 26 | Block 1 | 10.00 | 50.00 | 30.00 | 66.6 |
| 4 | 25 | Block 1 | 3.00 | 100.00 | 30.00 | 48.3 |
| 5 | 7 | Block 1 | 6.50 | 100.00 | 30.00 | 55.2 |
| 6 | 18 | Block 1 | 10.00 | 100.00 | 30.00 | 61.8 |
| 7 | 10 | Block 1 | 3.00 | 150.00 | 30.00 | 50.1 |
| 8 | 27 | Block 1 | 6.50 | 150.00 | 30.00 | 74.5 |
| 9 | 21 | Block 1 | 10.00 | 150.00 | 30.00 | 80 |
| 10 | 1 | Block 1 | 3.00 | 50.00 | 60.00 | 60 |
| 11 | 14 | Block 1 | 6.50 | 50.00 | 60.00 | 70 |
| 12 | 6 | Block 1 | 10.00 | 50.00 | 60.00 | 76.6 |
| 13 | 5 | Block 1 | 3.00 | 100.00 | 60.00 | 56.7 |
| 14 | 13 | Block 1 | 6.50 | 100.00 | 60.00 | 61.7 |
| 15 | 9 | Block 1 | 10.00 | 100.00 | 60.00 | 65 |
| 16 | 22 | Block 1 | 3.00 | 150.00 | 60.00 | 63.3 |
| 17 | 8 | Block 1 | 6.50 | 150.00 | 60.00 | 78.3 |
| 18 | 11 | Block 1 | 10.00 | 150.00 | 60.00 | 83.3 |
| 19 | 23 | Block 1 | 3.00 | 50.00 | 90.00 | 46.6 |
| 20 | 3 | Block 1 | 6.50 | 50.00 | 90.00 | 56.6 |
| 21 | 4 | Block 1 | 10.00 | 50.00 | 90.00 | 63.4 |
| 22 | 12 | Block 1 | 3.00 | 100.00 | 90.00 | 55.6 |
| 23 | 2 | Block 1 | 6.50 | 100.00 | 90.00 | 60.1 |
| 24 | 15 | Block 1 | 10.00 | 100.00 | 90.00 | 66.7 |
| 25 | 20 | Block 1 | 3.00 | 150.00 | 90.00 | 57.8 |
| 26 | 16 | Block 1 | 6.50 | 150.00 | 90.00 | 76.7 |
| 27 | 19 | Block 1 | 10.00 | 150.00 | 90.00 | 82.2 |

## Appendix E: Laboratories Analysis Pictures

Raw peanut shell

Ground RPS

Impregnated RPS



PS Ash after Pyrolysis

Final prepared AC after washed

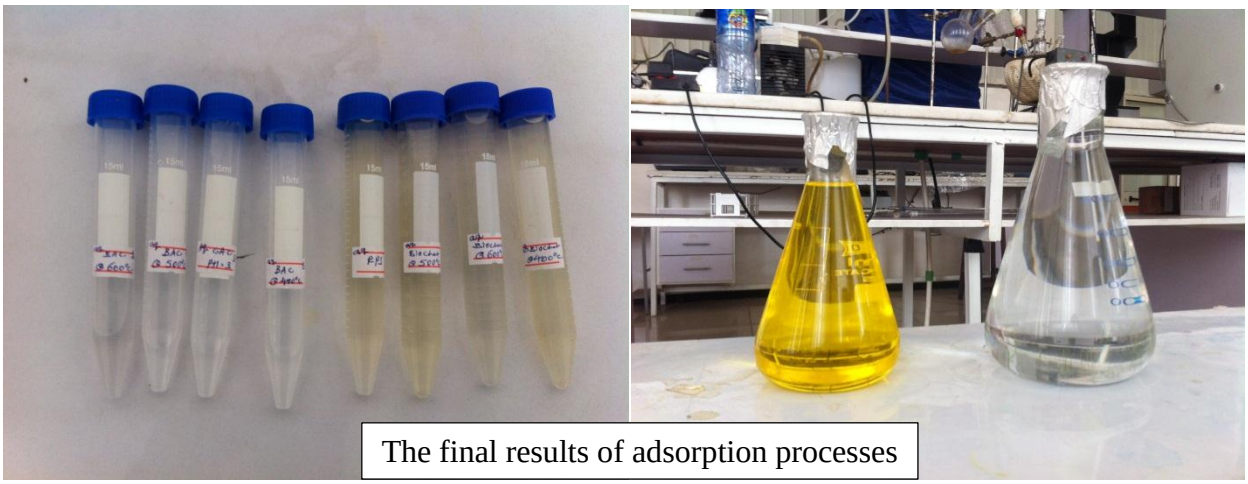
Golden Yellow 28 dye


Concentrated GY 28 dye solution

GY 28 Dye Solutions after Dilution

Preparation of solution based on specific parameters and ready for adsorption processes


After adsorption processes



The final results of adsorption processes

The residual AC after ad-sorption processes