# ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

## SCHOOL OF APPLIED NATURAL SCIENCE

## APPLIED CHEMISTRY PROGRAME

### REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING COFFEE HUSK ACTIVATED CARBON

**BY**

**BEKELE ABATE**

**A Thesis Submitted to Applied Natural Science Adama Science and Technology University in Partial Fulfillment for the Degree of Master of Science in Chemistry (Analytical Chemistry)**

**June, 2016**

**Adama, Ethiopia**

## ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

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I hereby certify that I have read and evaluated this Graduate project entitled **''REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING COFFEE HUSK ACTIVATED CARBON' '**prepared under my guidance by **Bekele Abate.** I recommend that it be submitted as fulfilling the Graduate project requirement.

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As members of the Board of Examiners of the Final M.Sc. Graduate project Open Defense Examination, I certify that I have read and evaluated the Graduate project prepared by **Bekele Abate** and examined the candidate. I recommend that the Graduate project be accepted as fulfilling the Graduate project requirement for the degree of Master of Science in Chemistry (Analytical Chemistry).

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# DEDICATION

I dedicated this project manuscript to my mother, Tsige Alemu for nursing me with affection, love and for her dedicated partnership in the success of my life.

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By my signature below, I declare and affirm that this Graduate project is my own work. I have followed all ethical and technical principles of scholarship in the preparation, data collection, data analysis and completion of this Graduate project. Any scholarly matter that is included in the Thesis has been given recognition through citation.

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# BIOGRAPHICAL SKETCH

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| AC | Activated Carbon |
| C.I | Class Index |
| CHAC | Coffee Husk Activated Carbon |
| GAC | Granulated Activated Carbon |
| IUPAC | International Union of pure and Applied Chemistry |
| MB | Methylene Blue |
| PAC | Powdered Activated Carbon |
| US.EPA | United States Environmental protection Agency |
| UV/Vis | Ultraviolet/Visible |

# REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING COFFEE HUSKACTIVATED CARBON

## ABSTRACT

*In this study coffee husk activated carbon (CHAC) was prepared and utilized as adsorbent to study its adsorption efficiency towards removal of methylene blue dye from aqueous solution. Activated carbon was prepared by acid treatment and carbonized at 500$^{o}$C for an hour. The amount of MB dye adsorbed was determined using UV-Vis spectrophotometer at its λ max of 663 nm. It was found that the adsorption of MB on the CHAC obeys both the Langmuir and Freundlich adsorption isotherms. The maximum adsorption capacity ('$Q_e$') and energy of adsorption ('b') were found to be 8.55 mg/L and 0.55 L/g, respectively as calculated from the Langmuir isotherm model. Values of the equilibrium parameter '$R_L$' from the Langmuir isotherm range between 0.022-0.083. Likewise the adsorption capacity of the adsorbent ('$K_f$') and the adsorption intensity ('n') were determined from the Freundlich isotherm and found to be 4.91 mg/g and 7.30, respectively. These results confirmed that the adsorption process of MB dye on the prepared adsorbent (CHAC) is favorable. The effects of some working parameters like pH, dye initial concentration, temperature and contact time on the adsorption of MB by CHAC were also studied. The results of pH effect reveal that the mini$^{i}$mum adsorption of the dye occurred at pH = 2 and the maximum at pH = 11. The dye adsorption was found to increase with increasing initial dye concentration and the percentage removal of the dye and the amount adsorbed on the surface of the adsorbent both showed significant increase with increase in temperature up to 35$^{o}$C. The effect of contact time on the percent removal of MB dye showed a decreasing trend as the dye initial concentration increased. Studies of the adsorption kinetics based on both the pseudo-second-order and the intra-particle diffusion models indicated that the diffusion of dye molecules onto the adsorbent surface could be the rate determining step for the mechanism of adsorption of MB on the CHAC.*

**Keywords**: Activated carbon, Adsorbate, Adsorbent, Adsorption, Methylene blue

# 1. INTRODUCTION

Environmental pollution is one of the serious problems facing humanity and other life forms, today. Environment can be polluted either naturally or through human activities. The term "Environment" refers to air, land, water, living things and environment created by human being (anthrosphere). Pollution is the releasing of contaminants into the environment that cause harm or discomfort to humans or other living organisms or that damage the environment. Human exposure to hazardous agents in the air, water, soil and food in the environment are major contributors to illness, disability and death worldwide. Furthermore, deterioration of environmental conditions in many parts of the world slows down sustainable development (Bhatnagar, 2004).

Water is one of the important components of the environment. In its pure form, water is tasteless, colorless and odorless. In this form, it is utilized by living organisms for sustenance and procreation or it is suitable for the intended purpose. Water is polluted by discharging of chemicals or biological materials that degrade the quality of the water and affects the organisms living in it. This process ranges from simple addition of dissolved or suspended solids to the discharge of the most insidious and persistent toxic pollutants such as pesticides, heavy metals, non-biodegradable chemical compounds for instance organic dyes (Pala, 2002)

Water pollution takes place at either the surface or underground levels. Underground water consists of water that has percolated below the topsoil. Surface water includes streams, rivers, oceans, run-offs, lakes, etc. Surface water is usually polluted through industrial waste water that contains inorganic and organic compounds in dissolved forms. Contamination of the environment from a variety of sources has become an increasingly serious problem in recent years. The release of dyes into wastewaters by various industries poses serious environmental problems due to the fact that various dyes are having persistent and recalcitrant nature. The presence of dyes in waterways is easily detectable even when released in small concentrations (Gucek, 2005). For some dyes, the dye concentration of less than 1 ppm in receiving water bodies is highly visible, so that even small quantities of dyes can color large water bodies.

This is not only aesthetically unattractive, but also may have an inhibitory effect on photosynthesis affecting aquatic ecosystems.

Dyes may be problematic if they are broken down anaerobically in the sediment, as toxic amines often produced due to incomplete degradation by bacteria (Weber, 1987).Some of the dyes or their metabolites are either toxic or mutagenic and carcinogenic (Chen, 2003).

The effluents from textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important sources of dye pollution. Many dyes and their break down products may be toxic for living organisms (Kannan, 2001).Synthetic dyes have complex aromatic structures which provide them physicochemical, thermal, biological, and optical stability (Seshadri, 1994).They require usually special treatment strategies. Recently, all governments have been under severe pressure by their people to stop dye-laden effluents to the public watercourses, unless it is treated properly. The U.S.EPA (United States Environmental Protection Agency) has classified textile wastes into four groups, dispersible, hard-to-treat, high-volume, and hazardous and toxic wastes (Arami, 2005). Basic dyes are the brightest class of soluble dyes used by the textile industry (R, 1996).Therefore, decolorization of dye is important aspect of wastewater treatment before discharge. It is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems ( (Kargi, 2004). Generally, biological aerobic wastewater treatment is not successful for decolorization of majority of dyes. Therefore, color removal was extensively studied with physico-chemical methods such as coagulation, ultra-filtration, electro-chemical adsorption and photo-oxidation (Bhattacharyya, 2005).

Among these methods, adsorption is by far the most versatile and widely used method for dye removal from wastewaters because of its initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances (Walker, 1998)). Granulated activated carbon (GAC) or powdered activated carbon (PAC) is commonly used for dye removal (Chern, 2001). However, these are expensive and their regeneration or disposal of secondary waste has several problems. Thus, a number of agricultural waste and by-products of cellulosic origin have been studied in the literature for their capacity to remove dyes from (Arami, 2005) aqueous solutions such as waste orange peel (Namasivayam, 1996), banana pith, cotton waste, rice husk (Ramakrishna, 1997) ,bentonite clay (Ozcan, 2004), powdered activated sludge (Bhattacharyya, 2005)

perlite (Dogan, 2004) , bamboo dust, coconut shell, ground (Otero, 2003)nut shell, rice husk, and straw (Kannan, 2001) , duck weed (Waranusantigul, 2003), sewage sludge (Chandran, 2002),barley husks, sugarcane bagasse, wheat straw, corncobs, tree ferns, wood chips, and corn-cob shreds. Therefore, there is a need for the search of low cost and easily available biomaterials, which can adsorb dyes from waste waters.

**Objectives of the Study**

The general objective of this work was:

To study the adsorption efficiency of activated carbon from coffee husk towards removal of methylene blue dye from aqueous solution by the batch adsorption method.

Accordingly, the following specific objectives were set**.**

i. To prepare activated carbon adsorbent from coffee husk for removal of methylene blue from aqueous solution.
ii. To evaluate the adsorption efficiency of the prepared activated carbon towards removal of methylene blue dye from aqueous solution.
iii. To investigate the effects of some working parameters such as: initial dye concentration, contact time, pH of the solution and temperature on the removal of methylene blue dye by the laboratory prepared activated carbon.

# 2. REVIEW OF LITERATURE

## 2.1. Dyes

Dyes are basically aromatic compounds. Their structures have aryl rings that have delocalized electron systems. These structures are said to be responsible for the absorption of electromagnetic radiation that has varying wavelengths, based upon the energy of the electron clouds. The complex aromatic molecular structure which make dyes more stable and difficult to biodegrade whether natural or synthetic dyes impart its color to colorize the materials by staining on it from a fine dispersion solution, sometimes with the help of mordant (fixing agent) (Yasmin, 2004). Synthetic dyes are extensively used in textile, carpet, printing, leather, paper, rubber, plastic, cosmetic, pharmaceutical and food industries to color their products because of their ease of use, inexpensive cost of synthesis, stability and variety of color compared with natural dyes ( (Verma, 2010) 2010; (Patil, 2011)). As dyes utilization in textile mills, paper, rubber, plastic, cosmetic, etc. increase the discharging of colored effluent to the nearby land or water bodies also increases. However, using of dyes for color the product materials have impact on the environment. For instance, malachite green dye is commonly used for the dyeing process and in the manufacturing of paints and printing inks (Chen, 2009). It is also used as a fungicide and antiseptic in aquaculture and fisheries. Despite its importance, malachite green is highly toxic to mammalian cells and also it affects the immune system and reproductive system as well as it has genotoxic and carcinogenic potentials (Srivastav, 2004).

### 2.1.1. **Colorant**

The dyes' adsorption ability of radiation is by the functional groups (Chromopores) present in dyes. The chromopores create the energy changes in the delocalized electron cloud of the dyes. This change makes the compound to absorb radiation within the visible range of colors. This absorption is recognized by human eyes and responds to the colors. The term "colorant" is used for the entire spectrum of coloring materials, including dyes and pigments. Dyes and pigments are sources of color, which are different from one another. Pigments are particles of color that are insoluble in water, oils and resins. They need a binder or dispersing agent to impart or spread their color. Dyes are usually water soluble and depend on physical or chemical reactions to impart their color.

Dyes are applied to numerous substrates for example to textiles, leather, plastic, paper and other substances whereas pigments are used for coloring paints, ink and cosmetics (Yasmin, 2004).

### 2.1.2. **Classification of dyes**

There are two practical ways to classify a dye

i. Application to materials (coloristic classification)
ii. Chemical structure (chemical classification).

According to their chemical classification, dyes can be classified into different groups based on the nature of their chromopore such as azo dyes, acridine dyes, diarylmethane dyes, triarylmethane dyes, indophenol dyes etc. As (Namasivayam, 2001)pointed out that dyes can be classified as anionic, cationic and nonionic. Anionic dyes are the direct acid and reactive dyes and cationic dyes are basic dyes, whereas nonionic dyes are dispersing dyes, because they do not ionize in an aqueous medium. The anionic and nonionic dyes have functional groups (chromopores) of azo or anthraquinone type.

### 2.1.3. **Dyes as organic pollutants**

Dyes are derivatives of aromatic compounds with a toxic effect since they are benzadine and other aromatic compound derivatives (Yasmin, 2004). Releasing of highly colored effluents to the nearby land or water bodies has negative impact on the environmental point of view such as aesthetically not attractive but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem by reducing photosynthetic activity. Some dyes or their metabolites are either toxic or mutagenic, allergic dermatitis, skin irritant, carcinogenic and causing direct destruction of aquatic communities (Namasivayam, 2001) (Arivolia, 2009). Dyes can also cause severe damage to human beings, such as dysfunction of kidney, reproductive systems, liver, brain, central nervous system, skin, lung and other respiratory disorders (Kadirvelu, 2003).

### 2.1. 4. **Methylene blue**

Methylene blue is a heterocyclic aromatic chemical compound which is most commonly used for coloring among all other dyes of its category. It is an important basic dye widely used for printing calico, printing cotton and tanning, indicating oxidation-reduction, and dyeing leather,

and in purified zinc-free form. It is also used as an antiseptic and for other medical purposes. Although not strongly hazardous, it can have various harmful effects. It causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. If swallowed, the dye causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting, and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions, tachycardia, and dyspnea, if inhaled. It is likely to cause irritation to the skin (Senthilkumaar, 2005). At room temperature it appears as a solid, odorless, dark green powder, which yields a blue solution when dissolved in water. Methylene blue is highly stable in the human body, and if ingested, it resists the acidic environment of the stomach as well as the many hydrolytic enzymes present. It is not significantly metabolized by the liver, and is instead quickly filtered out by the kidneys. Therefore, it is necessary to make sure the effluent contained methylene blue was treated first before it is released to environment (Bhattacharyya, 2005).

Methylene blue (C.I. number 52015) is basic dye and having molecular formula of $C_{16}H_{18}N_3SCl$ with molecular weight of 319.859 g/mol. At room temperature it appears as a solid, odorless, dark green powder. When hydrated it gives deep blue color. The chemical name of MB is 3,7-bis(Dimethylamino)-phenthiazin-5-ium chloride or Tetramethylthionine. The chemical structure of MB is shown in fig 1.

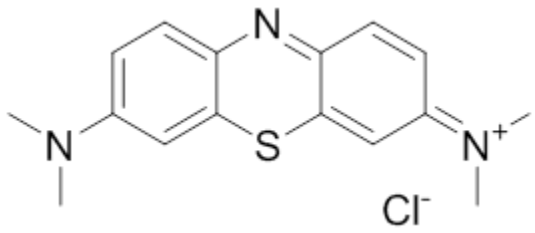


fig1. The chemical structure of methylene blue

**2.2. Treatment Methods for Industrial Dyes**

The removal of colored and colorless organic pollutants from industrial wastewater is difficult. This is due to their complex aromatic molecular structure and synthetic origin, which make them inert and non-biodegradable (Patil, 2011) Large number of researchers pointed out different methods to remove colored waste water effluents. Among those methods adsorption process has

been found to be superior technique and more effective method to remove colored waste water effluents (Verma and Mishira, 2010) (Verma, 2010).

(Hameed, 2005) Studied adsorption of MB onto bamboo-based activated carbon. Equilibrium adsorption and kinetics of MB dye on AC were examined at 30$^{o}$C. Adsorption isotherm of the MB on AC was tested by Langmuir and Freundlich adsorption isotherms. Kinetic models including pseudo-first-order and pseudo-second-order equation were selected to follow the adsorption process. The adsorption of MB could be best described by the pseudo-second-order equation.

(Nwabanne, 2009) Studied equilibrium uptake and sorption dynamics for the removal of a basic dye from aqueous solution using bamboo based activated carbon. Batch adsorption studies were carried out to evaluate the effect of various parameters such as pH, adsorbent dose, temperature and initial dye concentration. The pH of dye solution is one of the most important factors controlling the adsorption of dye onto adsorbent. The equilibrium data fitted very well to Langmuir and Freundlich models.

(Arivoli, 2010) Studied the potential use of activated carbon from morindabuch-ham bark carbon for the removal of dye in aqueous solution. The parameters studied include agitation time, dye initial concentration, carbon dose, pH and temperature. The adsorption followed first order reaction equation and the rate is mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm model were applied to the equilibrium data.

Experimental study of adsorption of MB from aqueous solution onto carbon nanotubes was investigated by (Shahryari, 2010). The adsorption kinetic data were analyzed using pseudo-first-order, pseudo-second-order and Elovich models. The kinetic parameters of this best-fit model was calculated and discussed.

(Theivarasu, 2011) Studied MB adsorption from an aqueous solution onto Ac prepared from cocoa (*Theobromacacoa*) shell. Adsorption kinetics and equilibrium were investigated as a function of initial concentration and contact time, pH and adsorbent dosage. Pseudo-first-order, pseudo-second-order and intra-particle diffusion models were used to examine the experimental data of different initial concentrations. Equilibrium data was analyzed using Langmuir,

Freundlich and Tempkin isotherm models. Kinetic studies indicated that the adsorption followed pseudo-second-order reaction.

(Venkatraman, 2011) Studied the ability of *TerminaliaCatapplinn*carbon to remove malachite green from aqueous solutions using different adsorbate concentrations by varying the amount of adsorbent, temperature, pH and shaking time.

(Yadav, 2011)Studied equilibrium and kinetic studies on adsorption of aniline dye onto activated rice husk carbon. AC was prepared by mixing the dried material with equal volumes of $H_2SO_4$ at room temperature and carbonized in muffle furnace kept at 500$^oC$ for an hour. Specific surface area of the AC was determined by sears methods (Sears, 1956). Effects of various parameters such as dye initial concentration, adsorbent dose, contact time and temperature have been investigated. The obtained data was analyzed in the light of Langmuir and Freundlich adsorption isotherms.

The potential use of low-cost natural Jordanian Tripoli for removal of a cationic dye from aqueous solution was studied by (Alzaydien, 2009) and different factors affecting adsorption such as, dye initial concentration, pH, contact time, adsorbent dose and temperature were evaluated. The equilibrium of adsorption was modeled by using Langmuir and Freundlich isotherm and maximum adsorption capacity was found to be 16.6 mg/g at 25$^oC$. The kinetic parameters and intra-particle diffusion were also used to determine for the adsorption system of MB on Jordan tripoli.

### 2.3. Use of Activated carbon as potential for Dye Removal

Activated carbon (AC) has been commonly used for the removal of organic dyes from industrial waste waters. In addition to its use for drinking water and waste water treatment, it is used today for many other purposes. Some other common uses are listed here: corn and cane sugar refining, gas adsorption, dry cleaning recovery processes, pharmaceuticals, fat and oil removal, electroplating, alcoholic beverages production.

AC has a wide range of amorphous carbon-based materials exhibiting a high degree of porosity, adsorption capacity, chemical stability and large surface area. These qualities make it an

excellent adsorbent characteristics and very useful for a wide variety of processes including filtration, purification, decolorization and separation.

AC can be produced by either chemical or steam activation. Carbonization converts the organic material to primary carbon, which is the mixture of ash, amorphous carbon and crystalline carbon. During activation, the internal surface becomes more highly developed and extended by controlled oxidation of carbon atoms. An AC has not only a highly developed internal surface area but also have accessibility to that surface via a network of pores of different diameters. Porosity is one of the criteria by which carbons are selected for a specific application because pore size affects the adsorption capacity of a given adsorbent. According to IUPAC, pore size can be categorized into three different groups. These are:

a. Micropores: pore diameter less than 2 nm
b. Mesopores: pore diameter range 2-50 nm
c. Macropores: pore diameter greater than 50 nm

All ACs contain micropores, mesopore and macropores within their structures but the relative proportions vary considerably according to the raw material (Ruthven, 1984). Mesopores do not generally play a large role in adsorption, except in particular carbons where the surface area attributable to such pores is appreciable (usually 400 $m^2/g$ or more). Whereas the micropore structure of an AC is the effective means of adsorption. Therefore, AC is not classified as a single product but rather of products suitable for a variety of specific applications. In practice, AC is found in two general forms (Bhatnagar, 2006)

i. Granular activated carbon (GAC)
ii. Powdered activated carbon (PAC)

GAC by definition is composed of particles size greater than 0.8 nm, about the size of coarse sand. PAC is composed of particles smaller than 0.8 nm. Exact specifications vary, but GAC is generally said to have larger pores and a smaller internal surface area. PAC is used for adsorption in liquid phase whereas GAC is used for adsorption of steam or gas phase.

The effectiveness of AC as an adsorbent is attributed to its unique properties including large surface area, a high degree of surface reactivity, universal adsorption efficiency and favorable

pore size. For comparison, a given type or sample of AC is usually quantified based on the following primary criteria:

i. Total surface area,
ii. Particle size distribution and
iii. Adsorptive capacity.

All these factors influence adsorption rate and capacity. Total surface area decides the extent of adsorption which is proportional to specific surface area. Specific surface area is an area per unit mass (g). Particle size distributions are important in carbon systems because the adsorption capacity of the adsorbent increased with decreasing particle size which is due to increase in the availability of active sites for adsorption (Sreenivasa, 2011).

### 2.4. Adsorption Process of Dyes

Adsorption is the transferring of adsorbate (dye) from the liquid phase onto the surface of a solid (adsorbent). Basically, there are two types of adsorption: (1) Physical adsorption (physisorption) and (2) Chemical adsorption (Chemisorption). Physical adsorption occurs when weak interparticle bonds exist between the adsorbate and adsorbent. Examples of such bonds are Van der Waals force. Whereas chemical adsorption occurs when strong interparticle bonds are present between the adsorbate and adsorbent due to exchange or sharing of electrons. Examples of such bonds are covalent bonds (Allen, 2005). The term adsorption is often confused with absorption. Absorption refers to a phenomenon where something is taken up through the bulk, such as a sponge absorbs water whereas adsorption refers to a phenomenon where something is taken up only at the surface, such as carbon powder adsorbs a dye. The general term for absorption and adsorption is sorption. A molecule that undergoes adsorption is referred to as the adsorbate, and the solid that adsorbs is the adsorbent (Itodo, 2010).

In adsorption process of dye on the solid surface, the dye species migrate towards the surface of the adsorbent. This type of migration proceeds till the existence of concentration gradient of the adsorbate species in the bulk of the solution to the surface of the adsorbent. Once equilibrium is attained, the migration of the solute species from the solution stops.

At this situation, it is possible to measure the magnitude of distribution of the solute species between the liquid and solid phases. This kind of distribution is a measure of the efficiency of the chosen adsorbent for the adsorption of particular solute (dye). When a powdered solid adsorbent is in contact with a solution containing dyes, the dyes first migrate from bulk of the solution to the surface of the liquid film. This surface exerts a diffusion barrier. This barrier may be very significant or less significant. The involvement of a significant quantum of diffusion barrier indicates the dominant role taken up by the film of diffusion in the adsorption process. Furthermore, the rate of an adsorption process is controlled either by external diffusion, internal diffusion or by both types of diffusions.

Adsorption isotherm is a functional expression for the variation of adsorption relative to the concentration of adsorbate in the bulk solution at constant temperature. It describes the relation between the adsorbate adhered by adsorbent and the adsorbate equilibrium concentration. The parameters that determine the shape of an isotherm are: adsorbent dose, pH, dye initial concentration, contact time and temperature. Adsorption isotherm can be expressed as Langmuir isotherm, Freundlich isotherm, Dubinin-Radushkevich, models, Tempkin models, etc. Langmuir and Freundlich isotherm models are well known for surface coverage studies (Itodo, 2010).

## 2.5. Adsorption Isotherms

The relationship between the amount of substance adsorbed at constant temperature and its concentration in equilibrium solution is called the adsorption isotherm. The equilibrium adsorption isotherms are of fundamental importance in the study of adsorption systems. The two well-known adsorption isotherm models for surface coverage studies are Langmuir and Freundlich isotherm models.

### 2.5.1. **Langmuir adsorption isotherm**

The Langmuir adsorption model is most commonly used to quantify the amount of adsorbate adsorbed on an adsorbent as a function of concentration at a given temperature.

Langmuir isotherm assumptions are:

1. Intermolecular forces decrease rapidly with increase of distance and consequently predict the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent.
2. Adsorption occurs at specific homogeneous sites within the adsorbent.
3. Once adsorbate molecule occupies active sites, no further adsorption can take place at that site.
4. All adsorption sites are identical and energetically equivalent.

Probability of one site being occupied is not dependent on the status of adjacent sites. Theoretically, the adsorbent has a finite number of sites for the adsorbate. Therefore, a saturation value is reached beyond where no further adsorption can occur. Linear forms of the Langmuir equations are (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_e} + \frac{1}{bQ_e} \qquad (1)$$

Where $q_e$ is the amount of dye adsorbed per unit mass of adsorbent (mg/g), $C_e$ is the equilibrium concentration of the adsorbate (mg/L),$Q_e$ and b represent maximum adsorption capacity and energy of adsorption, respectively. Langmuir parameters, $Q_e$ and b are determined from the slope and intercept of the linear plot $C_e/q_e$, versus $C_e$, respectively.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless separation factor or equilibrium parameter, $R_L$ which is defined by:

$$R_L = \frac{1}{1 + bC_o} \qquad (2)$$

Where, $C_o$ is the initial concentration of the adsorbate in solution, b the Langmuir's adsorption constant (L/mg). The value of $R_L$ indicates the type of the isotherm to be either unfavorable ($R_L > 1$, linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Nwabanne, 2009).

### 2.5.2. **Freundlich adsorption isotherm**

The Freundlich isotherm equation takes into account repulsive interactions between adsorbed solute particles and also account for surface heterogeneities. The equation is adequate to describe

non-linear adsorption in narrow range of adsorbate concentration. The logarithm form of the Freundlich isotherm is given as follows (Freundlich, 1906):

$$\log q_e = \frac{1}{n}\log C_e + \log K_f \qquad (3)$$

Where $q_e$ is the amount of dye adsorbed at equilibrium, $C_e$ is the concentration of dye solution at equilibrium, $K_f$ and 1/n is empirical constant indicates adsorption capacity of the adsorbent and adsorption intensity, respectively. Their values can be obtained from the intercept and slope of linear plots of log $q_e$ versus log $C_e$. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1), unfavorable (1/n > 1) (Bell, 1998).

The equilibrium adsorption capacity, $q_e$ (mg/g) can be calculated using the mass balance equation given (Nwabanne and Mordi, 2009) (Nwabanne, 2009).

$$q_e = V\frac{(C_o - C_e)}{W} \qquad (4)$$

Where $C_o$ and $C_e$ are the initial and final equilibrium concentration of adsorbate (mg/L), V is volume of the solution (L) and W is the dry adsorbent (g).The amount of adsorbate adsorbed, $q_t$ (mg/g) at any time can be calculated using Equation (5):

$$q_t = V\frac{(C_o - C_t)}{W} \qquad (5)$$

Where, $C_t$ is the concentration of adsorbate, (mg/L) at any time.

The percentage removal of adsorbate can be calculated using the following relationship (Shahryari, 2010).

$$\% \text{ removal of MB} = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (6)$$

Where $C_o$ and $C_e$ are the initial and final equilibrium concentration of adsorbate, (mg/L). The applicability of two adsorption isotherm (Langmuir and Freundlich) can be compared by evaluating the multiple regression correlation coefficients, $R^2$. In regression, the $R^2$ coefficient of determination is a statistical measure of how well the regression line approximates the real data

points. $R^2$ is a number between zero and one that would give some information about the best fit of a model. If the value of $R^2$ close to zero suggests a poor model. If the value of $R^2$ is 1.0 indicates that the regression line perfectly fits the data. If the Value of $R^2$ occurs outside the range 0 to 1, it is used to measure the agreement between observed and modeled value (Abdi, 2002).

### 2.5.3. **Kinetics of adsorption**

The study of adsorption kinetics describes the rate of uptake of the adsorbate molecule onto adsorbent, which determines the residence time required for design adsorption systems. This rate depends on the physico-chemical characteristics of the adsorbate and adsorbent, pH of the solution, temperature and concentration of the solution (Schimmel, 2010). The adsorption kinetics show the evaluation of the adsorption capacity through time and it is necessary to identify the adsorption mechanism in a given system. The following models are used to describe the adsorption kinetics behavior.

#### 2.5.3.1. **Pseudo-first-order equation**

The adsorption kinetic described by the Lagergren pseudo-first-order equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expressed as follows (Shahryari, 2010):

$$\frac{dq_t}{d_t} = K_1(q_e - q_t) \qquad (7)$$

Where $q_e$ and $q_t$ refers to the amount of dye adsorbed per unit mass of the adsorbent at equilibrium time and any time, (mg/g), respectively and $K_1$ is the rate constant of pseudo-first-order adsorption ($min^{-1}$).

Integrating Equation (7) by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ gives:

$$\log \frac{q_e}{(q_e - q_t)} = \frac{K_1 t}{2.303} \quad (8)$$

Equation (8) can be rearranged to obtain the following linear form:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (9)$$

The rate constant, $K_1$ and equilibrium adsorption capacity, $q_e$ can be predicted from the slope and intercept of the linear plots of log ( $q_e - q_t$ ) versus t, respectively.

2.5.3.2. **Pseudo-second-order equation**

The adsorption kinetic may also be described by the pseudo-second-order equation. The rate of pseudo-second- order equation is dependent on the amount of solute adsorbed on the surface of adsorbent and the amount adsorbed at equilibrium. The differential equation is generally given as follows (Shahryari, 2010):

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)2 \quad (10)$$

Where $K_2$ is the rate constant of the pseudo-second-order equation (g/mg.min) and $q_e$ is equilibrium adsorption capacity (mg/g).

Integrating Equation (10) by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ is simplified and rearranged to obtain linearized equation.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e 2} \quad (11)$$

The values of $q_e$ and $K_2$ can be determined experimentally from the slope and intercept of the plots of $t/q_t$ versus t, respectively.

2.5.3.3. **Intra particle diffusion equation**

The adsorbate species are most probably transported from the bulk of solution into the solid phase through intra-particle diffusion (transport process), which is often the rate-limiting step in many adsorption processes. The nature of the rate limiting step in adsorption system can also be assessed from its aqueous solution to the adsorbent by intra-particle diffusion. Therefore, to investigate whether there is a possibility of adsorption of the adsorbate to diffuse into the interior pores of the adsorbent or not, intraparticle diffusion can be explored by using Weber and Morris equation (Weber, 1963).

$$q_t = k_i (t)^{1/2} + C \quad (12)$$

Where, $q_t$ is the amount of dye adsorbed at time t, (mg/g), $k_i$ is intra-particle diffusion rate constant (mg/g.min$^{1/2}$) and C is intercept. The value of $k_i$ and C are obtained from slope and intercept of the linear plot of $q_t$ versus $(t)^{1/2}$ at different dye initial concentrations at fixed temperature. The magnitude of the intercept, C is a measure of the thickness of adsorbed layer which gives an idea about the thickness of boundary layer. i.e., the larger the intercept, the greater is the boundary layer effect (Arivoli, 2010).

# 3. MATERIALS AND METHODS

## 3.1. Study Site and Descriptions

Synthesis of activated carbon adsorbent and all batch adsorption experiments were carried out at Ethiopian Sugar Corporation Research and Training Center, Research Laboratory.

## 3.2. Materials and Apparatus

### 3.2.1. **Instruments and apparatus**

Instruments used in this study include: pH meter (mettler Toledo Mp220), electronic balance (OHAUS Switzerland), hot air oven (Contherm 260M), volumetric flasks (PYREX, UK), beakers, shaker (Orbital Shaker SO1, UK), centrifuge ($K_2$ Series, CENTRION SCINTIFIC LTD West Sussex, UK), thermostatic water bath (Grant Model SBB14, England), deionizer (ELGANACAN, Cartridge type C114, UK) muffle furnace (BiBBY, Stuart), quartz cuvette, pipette, graduated cylinder, conical flasks, thermometer, mortar and pestle, ceramic crucible, evaporating dish, deionizer separatory funnel, Whatman No.1 filter paper, desiccator, taste tubes and UV/vis spectrophotometer(SANYO SP65 GALANAKAMP, UK).

### 3.2.2.**Chemicals and reagents**

Chemicals used in this research include concentrated sulphuric acid (98.08%), hydrochloric acid (35-38%), sodium chloride (99.5%), sodium bicarbonate (99.5-101%), distilled water, methylene blue (MW 319.859 g/mol basic blue 9), deionized water for preparing various concentrations of MB dye and all other reagents for other purposes including removal of dirt particles, water soluble materials and excess acids from the adsorbent material.

### 3.3 Methods and Procedures

#### 3.3.1. **Collection of coffee husk samples**

Sufficient quantity of coffee husk that was used for preparation of activated carbon powder adsorbent was obtained by purchasing from the local market in Shashamane of the Eastern Arsi zone of the Oromia Region, Ethiopia. Clean polyethylene plastic bags were used to carry the coffee husk samples to the Research Laboratory of the Ethiopian Sugar Research Center laboratory, Wonji

#### 3.3.2. **Preparation of activated carbon from coffee husk**

The coffee husk samples were dried in sunlight until they became moisture free. The samples collected from different markets were mixed together uniformly to get a composite sample. This sample was washed several times with distilled water to remove dirt particles and any water soluble materials present and then kept in air oven at $90^0$C for 12 h. The clean and dried coffee husk sample was crushed using mortar and pestle and then sieved to obtain a fine powder of uniform particle size. After transferring the powder to a 250 mL beaker, it was soaked with sufficient amount of conc. $H_2SO_4$and left overnight at room temperature. The acid treated husk powder was then washed thoroughly with distilled water and then filtered off with Whatman No.1 filter paper. The residue was transferred into a clean beaker, to which enough amount of 0.2 M $NaHCO_3$solution was added and soaked again overnight so that any excess acid present was neutralized. The treated solid residue was washed again with distilled water till attaining a constant pH and then made to dry at room temperature. The powder obtained as such was kept in a hot air oven at $120^0$C for a day and then further heated for 1 h in a muffle furnace that was set to $500^0$C at controlled temperature (Javier. et. al,. 2011). The resulting material, which was technically referred to as an activated carbon (AC) form of coffee husk was cooled and grounded to fine powder with mortar and pestle and finally screened through a set of sieves of mesh size less than 250µm (stainless steel) and stored in a desiccator until further use (Arivoli, 2010).

### 3.3.3. **Determination of the physico-chemical properties of the adsorbent (CHAC)**

#### 3.3.3.1. **Determination of the moisture content of the adsorbent**

One gram of adsorbent was weighed accurately in an evaporating dish and placed in an electric oven at 120$^{o}$C for 12 h. It was then cooled and weighed again. The process of heating, cooling and weighing of the material was repeated several times at 30 min intervals until the difference between two consecutive weighing became less than 0.01 g (Renugadevi, 2011). The moisture content was determined using equation given 13:

$$\text{Moisture content by weight} = \frac{(M - X)}{M} \times 100 \qquad (13)$$

Where M is weight of the adsorbent taken for the test and X is weight of the adsorbent after drying both in grams.

#### 3.3.3.2. **Determination of the ash content**

Accurately weighed, 1g adsorbent was kept in a porcelain crucible and placed in an electric oven at 120$^{o}$C for 12 h. The crucible was then removed from the oven and heated in a muffle furnace at a temperature of 500$^{o}$C for 1 h. The crucible with its content was removed from the furnace and cooled to room temperature and weighed (Renugadevi, 2011).

$$\text{Ash content percent by weight} = \frac{M_1}{(M_2 - X)} \times 100 \qquad (14)$$

Where $M_1$ is weight of the ash (g), $M_2$ is weight of the adsorbent taken for the test (g) and X is moisture content present in the material taken for test.

#### 3.3.3.3. **Determination of the point of zero charge of the adsorbent**

Initial pH values of the aqueous solutions were adjusted to 2-11 with an interval of 15 minute either by adding a few drops of 0.1 M NaOH or 0.1 M HCl solution by using a pH-meter. To each solution 0.2 g of the CHAC was added to 200 mL solution of 0.1 M NaCl. The solution mixture was allowed to equilibrate in reciprocating shaker at 250 rpm at room temperature for 60 min. Then the suspension of carbon so present in the mixture was separated by centrifugation at 250 rpm for 5 min and the final pH measured again.

The results are plotted with pH final minus initial against pH final. The point at which pH = 0 is known as point of zero charge (Sreenivasa, 2011).

### 3.3.3.4. Specific surface area of coffee husk activated carbon

The surface area of the coffee husk activated carbon (CHAC) was determined using the method described by (Yadav, 2011). About 1 g of the sample was mixed with 100 mL of deionized water and 20 g NaCl. The mixture was stirred for 5 min after the final volume of the solution was made up to 150 mL with 0.1 M HCl, its final pH was adjusted to 4. This mixture was then titrated against 0.1 M NaOH to raise the pH from 4 to 9 and the volume of 0.1 M NaOH consumed for the titration was measured in triplicate and the average value was taken for the surface area calculation. To this effect, the specific area (i.e. area per unit mass (g)) of the adsorbent was calculated by the Sears Method using the formula (Sears, 1956).

$$S = 32V - 25 \quad (15)$$

Where S = Surface area of adsorbent per gram ($m^2/g$), V= volume of 0.1M NaOH required to raise the pH of the sample from 4 to 9.

### 3.3.4. Preparation of adsorbate solution

A stock solution of MB was prepared by dissolving the dye with deionized water. 1 g of MB was weighed accurately and transferred into 1000 mL Volumetric flask to which deionized water was added first in small amount to dissolve it completely and then to make up the final solution to 1 L mark. The resultant solution contained 1000 mg/L of MB. A series of working solutions of different concentrations were prepared by diluting the stock solution of MB with deionized water.

### 3.3.5. Studies on the batch mode adsorption of MB on CHAC from aqueous solution

The experiments on the adsorption of MB on coffee husk activated carbon was carried out in reciprocating shaker at 250 rpm using 250 mL conical flasks containing aqueous solutions of the dye in concentration of 20, 40, 60, and 80 mg/L. To the resulting solution, 0.2 g of the adsorbent was added to each flask containing 50 mL of the dye solution at a neutral pH and room temperature.

The initial pH value of each solution was adjusted with 0.1 M HCl or 0.1 M NaOH using a pH meter. In all experiments the flasks were sealed to prevent any change in volume during the experiment. After shaking the flaks, samples were withdrawn at 15 min intervals from the flasks and each time the dye solution was first separated from the adsorbent by centrifuging at 250 rpm for 10 min. Concentration of each MB solution free of the suspended carbon was estimated by measuring its absorbance at 663 nm using UV-Vis spectrophotometer. The values of percentage removal and amount of MB adsorbed at equilibrium $q_e$ (mg/g) were then calculated using the Langmuir and Freundlich isotherm models. The effects of various parameters such as dye initial concentration, contact time, pH, and temperature were studied.

### 3.3.6. **Effects of various parameters on the adsorption of MB by CHAC**

#### 3.3.6.1. **Effect of pH**

The effect of pH was studied at the pH values of 2-11 at the interval of each time using 50 mL MB solution with a fixed concentration of 20 mg/L and by treating it with 0.2 g of the adsorbent at room temperature. The acidic and alkaline pH of the media was maintained by adding 0.1 M HCl and 0.1 M NaOH solutions using a pH meter. After shaking the flasks for 25 min, the samples were withdrawn from the flasks and the dye solutions were separated from the adsorbent by centrifugation at 250 rpm for 10 min. Concentration of MB solution free of suspended carbon was estimated by measuring its absorbance at 663 nm using UV-Vis spectrophotometer. While carrying out the pH experiments the parameters such as contact time, temperature, agitation speed, particle size, volume of adsorbate and adsorbent dosage were kept constant. Finally, the amount adsorbed and percent removals of MB dye were calculated and the plot of percent removal of MB dye versus pH was plotted.

#### 3.3.6.2. **Effect of initial dye concentration**

The effect of initial dye concentrations on the extent of adsorption of MB on the prepared CHAC adsorbent was studied by taking 50 mL of the diluted stock solutions of MB containing of 20, 40, 60, and 80 mg/L using 0.2 g of the adsorbent at each time. After shaking the flasks for 25 min, samples were withdrawn from the flasks and the dye solution was separated each time from adsorbent by centrifuging it at 250 rpm for 10 min.

Concentration of MB solution free of any suspended carbon was estimated by measuring its absorbance at 663 nm using UV-Vis spectrophotometer. All other parameters were kept constant. Amount adsorbed and percent removal of MB dye was then calculated and the plot of percent removal of the dye versus initial concentrations of the dye was plotted.

3.3.6.3. **Effect of temperature**

The effect of temperature was evaluated at three different temperatures viz., 25, 30, and 35$^{o}$C (controlled with a thermostatic bath) by taking 50 mL of MB solutions with initial concentrations of 20, 40, 60, and 80 mg/L and using 0.2 g of the adsorbent in each case. After shaking the flasks for 25 min, samples were withdrawn from the flasks at intervals each time the dye solution being separated from the adsorbent by centrifuging it at 250 rpm for 10 min. Concentration of MB solution free of any suspended carbon was estimated by measuring its absorbance at 663 nm using UV-Vis spectrophotometer. All other factors were kept constant. Amount adsorbed and percent removals of MB dye were calculated. The graph of percent removal and amount adsorbed versus initial concentrations at different temperatures were plotted.

3.3.6.4. **Effect of contact time**

The effect of contact time was studied by taking 50 mL of MB solution with initial concentrations of 20, 40, 60, and 80 mg/L each time using 0.2 g of the adsorbent. Adsorption studies of MB dye on the coffee husk activated carbon was carried out for 10-60 min. at the interval of 10 min. All other factors such as temperature, agitation speed, pH, volume of the adsorbate, particle size and adsorbent dosage were kept constant. Finally, the amount adsorbed and percent removals of MB dye versus contact time were plotted.

3.3.7. **Kinetic studies on batch mode adsorption of MB by CHAC**

A 0.2 g adsorbent was added in each of four 250 mL conical flasks each containing 50 mL of MB solution to give four different initial concentrations 20, 40, 60, and 80 mg/L, respectively. The flasks were sealed to prevent any change in volume during the experiment maintaining a neutral pH and room temperature. After shaking the flasks, samples were withdrawn at 15 min intervals from the flasks and the dye solution was freed from any suspended material by centrifuging it at 250 rpm for 10 min.

Concentration of MB solution free of suspended carbon was estimated by measuring its absorbance at 663 nm using UV-Visible spectrophotometer. Rate and kinetic order of adsorption of MB on the coffee husk activated carbon were determined.

3.3.8. Data analysis and interpretation

All data generated from the above experiments were analyzed using the Microsoft Excel, Window program and the linear regression values were computed as required.

# 4. RESULTS AND DISCUSSON

## 4.1.Physico-Chemical Characteristics of Coffee Husk Activated Carbon

Activated carbon is widely used as an adsorbent due to its high adsorption capacity, high specific surface area, micro porous structure and high chemical and mechanical stability. The physico-chemical characteristics of the adsorbent determine rate and adsorption capacity. The physico-chemical properties of the chosen adsorbent are listed in Table1 below.

Table1. Characteristic parameters of coffee husk activated carbon.

| Properties | Values |
|---|---|
| Particle size (µm) | < 250 |
| Moisture content (%) | 1.16 |
| Surface area ($m^2/g$) | 86.2 |
| Ash content (%) | 3.50 |
| $pH_{pzc}$ | 6.52 |

## 4.2. Adsorption Studies

The experimental data were analyzed in the light of the Langmuir and Freundlich isotherms described in the literature section (2.5.1 and 2.5.2, respectively). The plot of $C_e/q_e$ versus $C_e$ gave straight line (Figure 2), indicating that adsorption of MB dye on the CHAC follows the Langmuir isotherm. The Langmuir constants '$Q_e$' and 'b' were determined from this isotherm and their values were provided in Table 2. The fact that experimental data fits in the Langmuir isotherm may be due to the homogeneous distribution of the active sites on the CHAC surface, since the Langmuir isotherm assumes that the surface is homogeneous. The maximum monolayer adsorption capacity '$Q_e$' of CHAC was found to be 8.55 mg/g. From this value it has been concluded that the adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy (McKay, 1992).

To confirm the favorability of the Langmuir adsorption process, the separation factor 'RL' values at different adsorbate initial concentrations were calculated (Table 2). The 'RL' values lie between 0 and 1 which confirm that the adsorption process of MB dye on activated carbon prepared from coffee husk is favorable (Nwabanne, 2009)

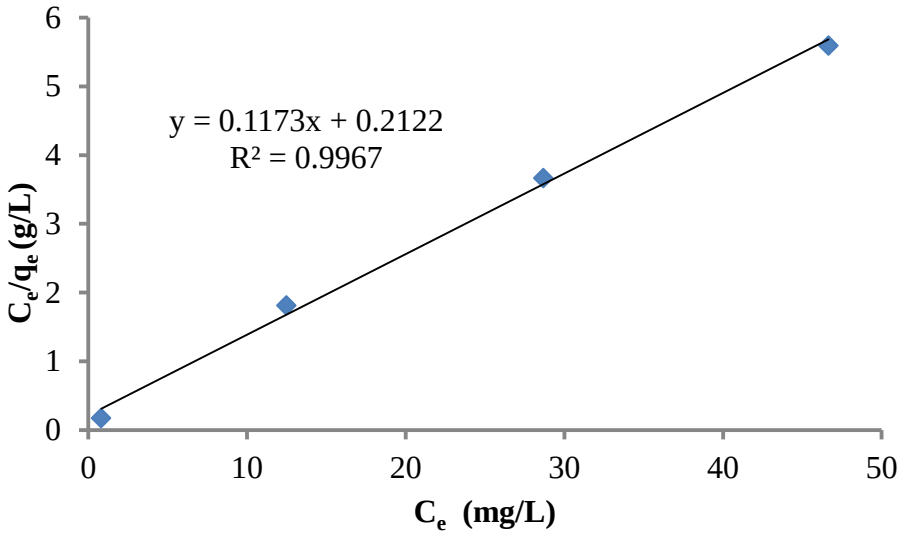


Figure 2.Langmuir adsorption isotherm for MB on CHAC.

Table 2. Results of the Langmuir and Freundlich adsorption isotherms studies at room temperature for adsorption of MB dye on CHAC.

| Adsorption isotherm | Statistical parameters/constants | | | |
|---|---|---|---|---|
| | $Q_e$(mg/g) | b (L/mg) | $R^2$ | $R_L$ |
| Langmuir | 8.55 | 0.55 | 0.996 | 0.022-0.083 |
| | $K_f$ (mg/g) | N | $R^2$ | |
| Freundlich | 4.91 | 7.30 | 0.999 | |

Figure 3 clearly reveals that the plot of log $q_e$ versus log $C_e$ is linear as described in the literature (section 2.5.2 equation 3)from which the Freundlich constants 'n' and '$K_f$' were calculated from the slope and intercept, respectively, and the results are given in Table 2. The value of 1/n which was found between 0 and 1 indicates that the Freundlich isotherm is also favorable and heterogeneous system (Bell, 1998).

However, the adsorption is not restricted to a monolayer formation but the model predicts that dye concentration on the adsorbent increases with increase in dye concentration in the solution. Theoretically, adsorbent has finite number of sites and once all these sites are occupied by the adsorbate molecules further adsorption cannot take place. The applicability of Langmuir and Freundlich adsorption isotherms were compared by evaluating the correlation coefficients ($R^2$). As it can be seen from Table 2, a high $R^2$ value of 0.999 was obtained in case of the Freundlich model while the $R^2$ for Langmuir model was 0.996. This indicates that the Langmuir model seems to be more suitable for describing the adsorption equilibrium of MB on CHAC. Thus it is reasonable to conclude that the adsorption of MB on CHAC involves homogeneous adsorption sites which are similar to each other in respect of adsorption phenomenon. Similar result was reported by Nwabanne and Mordi (2009) (Nwabanne, 1555-1559) for applicability of Langmuir model for adsorption of basic dye on bamboo. A direct comparison of literature data obtained using different adsorbents may not be appropriate since experimental conditions are by no means systematically the same. However, the adsorption capacity '$Q_e$' of the adsorbent used in the present study is 8.55 mg/g and this can be compared with those obtained from the literature as indicted in Table 3.

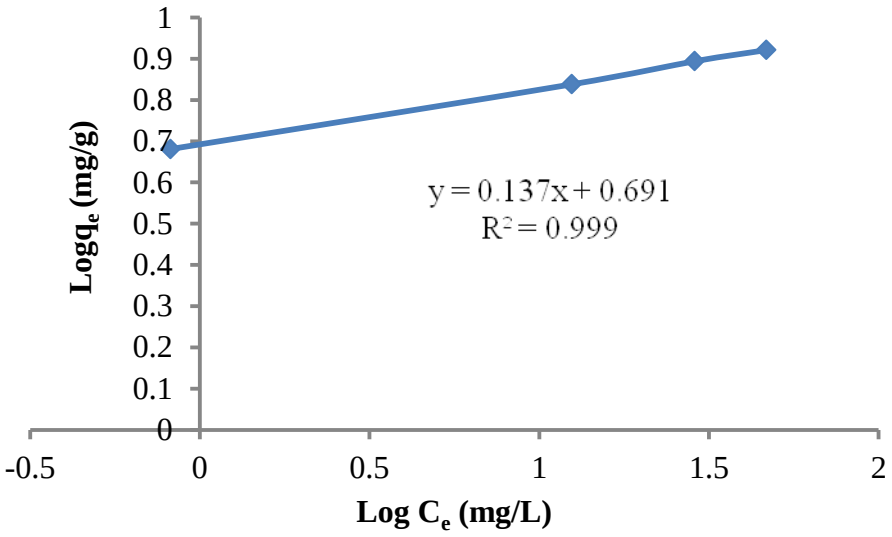


Figure 3.Freundlichadsorption isotherm for MB on CHAC.

Table 3. Comparison of adsorption capacity of MB dye with other adsorbents.

| Adsorbent | Qe (mg/g) | References |
|---|---|---|
| Chrome sludge | 0.51 | Lee *et al*.,1996 |
| Fly ash | 1.3 | Woolard *et al*., 2002 |
| Activated date pits (500$^{o}$C) | 12.9 | Benat*et al*., 2003 |
| Natural Jordanian tripoli | 16.6 | Alzaydien, 2009 |
| Akashkinari coal (20$^{o}$C) | 2.123 | Khan *et al*., 2004 |
| Akashkinari coal (30$^{o}$C) | 1.785 | Khan *et al*., 2004 |
| Coffee husk activated carbon (500$^{0}$C) | 8.55 | Present work |

4.2.1. **Effects of various parameters**

4.2.1.1. **pH**

The pH of the dye solution plays an important role in the whole adsorption process; particularly on the adsorption capacity. A useful index that indicates whether the adsorbent surface is likely to become negatively or positively charged as a function of the pH is that the pH value at which the net electric charge of the surface is zero. This value is called the point of zero charge ($pH_{pzc}$) or the pH value of isoelectric point of zeta potential (ZIEP) (Geethakarthi, 2011). At pH value lower than the $pH_{pzc}$ (pH <$pH_{pzc}$), the carbon surface has a net positive charge, while at pH value higher than the $pH_{pzc}$ (pH >$pH_{pzc}$) the surface has a net negative charge (Al-Deg. Y, 2000). From Figure 4, $pH_{pzc}$ of CHAC is 6.52. Therefore, the adsorption of the cationic dyes at pH <$pH_{pzc}$ is unfavored, whereas at pH >$pH_{pzc}$ the adsorption of cationic dyes is favored. Similar behavior of adsorption of cationic dyes onto low cost acid activated carbon was reported by (Venkatraman, 2011). The result of effect of pH on the adsorption of MB dye on CHAC is presented in Figure 4. The result reveals that the selected adsorbent showed good adsorption capacity more in basic medium than in acidic medium. This may be attributed to the cationic nature of the AC which led to adsorb hydrogen ions ($H^{+}$) on the surface of it when immersed in water and make it positively charged. From Figure 5, (Plot of percent removal of MB dye versus pH on CHAC at contact time = 30 min, initial dye concentration = 20 mg/L, adsorbent dosage = 0.2 g/50 mL of MB solution, agitation speed = 250 rpm, particle size < 250 µm and temperature = 24 $\pm$ 1$^{o}$C), It is evident that the optimum removal of color was observed at pH = 11 and minimum at pH = 2.

At pH = 2 the removal was minimum but it increased along with increasing initial pH of the dye solution from 2 to 11. The observed increase in adsorption of MB dye at higher pH may suggest that the carbon surface is negatively charged which favor adsorption of cationic dye on the available sites. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged cationic dye due to electrostatic repulsion (Shahryari, 2010). At pH = 2 lowest adsorption of MB dye may be occurred because the surface of CHAC is positively charged which lead to an increase in hydrogen ion concentration which compete with the positively charged carbon surface and adsorption of the positively charged dye decreases because of reduction in the force of attraction between adsorbate and adsorbent (Ponnusami, 2009). Moreover, the increase in the adsorption of MB dye with increasing of pH value is also due to electrostatic attraction between cationic dye and excess $OH^-$ ions in the solution. Some researchers have reported that adsorption of MB on AC usually increases as the pH is increased (Gupta, 2004); (Arivoli, 2010).

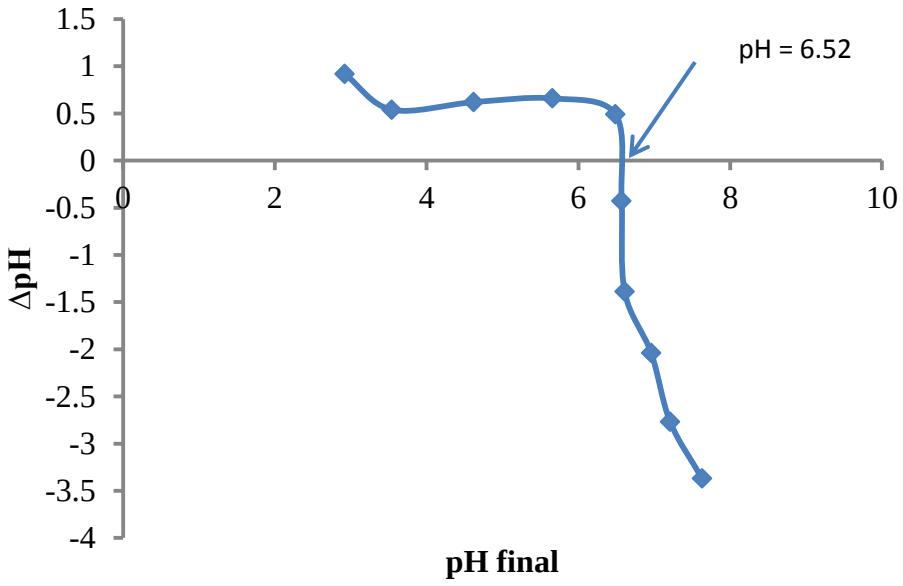


Figure 4.Plot of ΔpH versus pH final of CHAC.

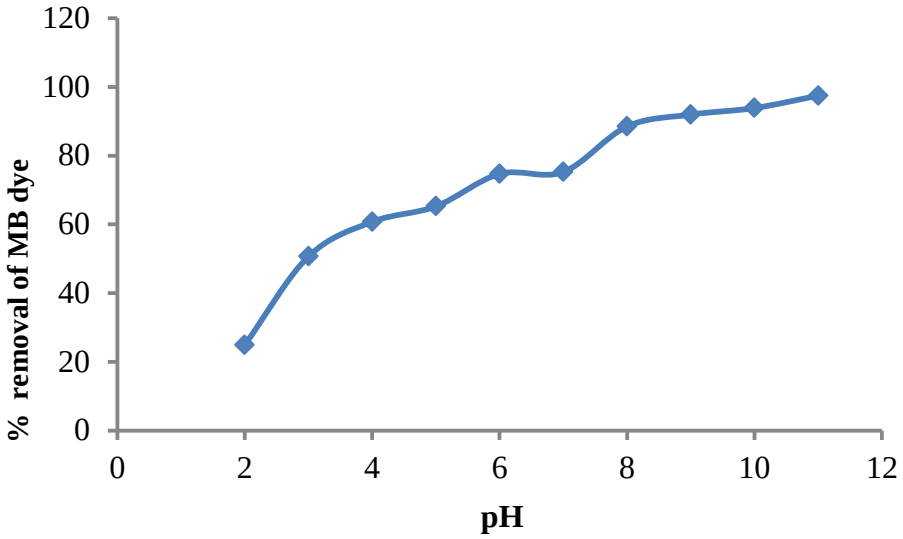


Figure 5. Plot of percent removal of MB dye versus pH on CHACat contact time = 30 min.

4.2.1.2. **Initial concentration of MB**

Initial concentration of adsorbate has its own importance in adsorption process and variation in its concentration shows significant effect. The result of effect of initial concentrations of MB dye adsorption on adsorbent is presented in Figure 6, (Plot of percent removal of dye versus initial concentration of MB dye on CHAC at pH = 11, adsorbent dosage = 0.2 g/50 mL of MB solution, contact time = 30 min, agitation speed = 250 rpm, particle size < 250 µm and temperature = 24 $\pm$ 1$^{o}$C). The result indicates that the MB dye removal decreases from 68.70 to 30.79% while the amount adsorbed increases from 3.435 to 6.158 mg/g with increase of dye initial concentration (Appendix Table 5). These results may be explained by the fact that at low adsorbate concentration, the ratio of surface active sites to total MB molecule is high; hence the MB ions could interact with the adsorbent to occupy the active sites on the carbon surface sufficiently and can be removed from the solution (Poots. VJP., 1976). But at higher initial concentration of the MB dye, the number of available active sites per MB dye molecule at the adsorbent surface becomes fewer resulting decrease in the removal of MB dye. However, the total amount of the dye adsorbed per unit mass of the adsorbent increases with increase in the dye initial concentrations (Yadav, 2011). A similar trend was also observed for MB adsorption onto carbon nanotubes (Sreenivasa, 2011) bamboo-based activated carbon (Hameed, 2005) and morinda coreiabuch-ham bark (Arivoli, 2010).

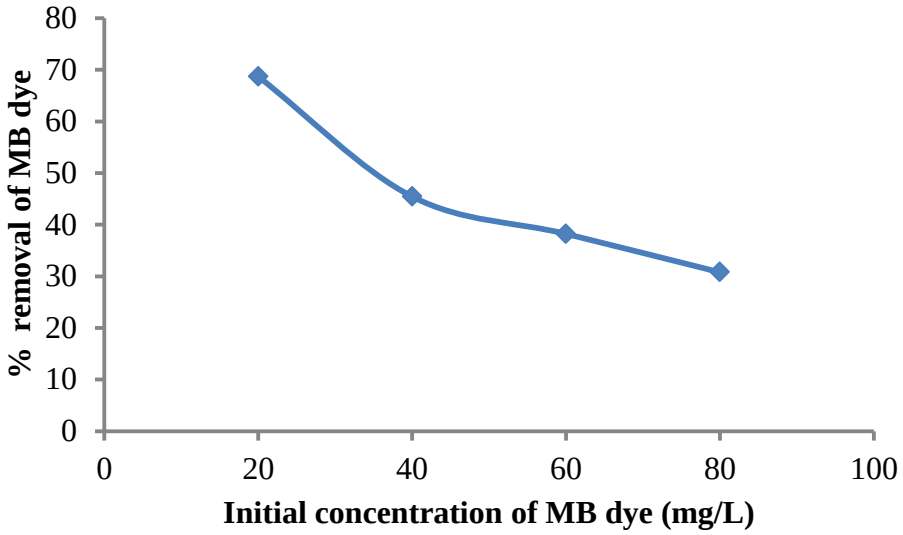


Figure 6. Plot of percent removal of dye versus initial concentration of MB dye on CHAC at pH = 11.

4.2.1.3**. Temperature**

The result of effect of temperature on adsorption of MB on CHAC is presented in Figures 7, (Plot of amount adsorbed versus initial concentration of MB dye on CHAC at pH = 11, adsorbent dosage = 0.2 g/50 mL of MB solution, contact time = 30 min, agitation speed = 250 rpm, particle size < 250 µm, temperature = 25$^{o}$C, 30$^{o}$C and 35$^{o}$C). andFigure8, (Plot of percent removal of MB dye versus initial concentration of the dye by CHAC at pH = 11 adsorbent dosage = 0.2 g/50 mL of MB solution, contact time = 30 min, agitation speed = 250 rpm, particle size < 250 µm, and temperature = 25$^{o}$C, 30$^{o}$C and 35$^{o}$C). The result indicates that the percent removal of the adsorbate on the adsorbent and adsorption capacity of the adsorbent increased with increase in temperature of the system from 25$^{o}$C to 35$^{o}$C (Appendix Table 6). This may be a result of increase in the mobility of the large MB ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the AC enabling large MB ion to penetrate further (Dogan and Alkan, 2003). The enhancement of adsorption capacity of the AC at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface. The greater removal of MB dye

due to increasing temperature may be also attributed to chemical reaction taking place between the functional groups of the adsorbent (Hiroyuki, 1994).

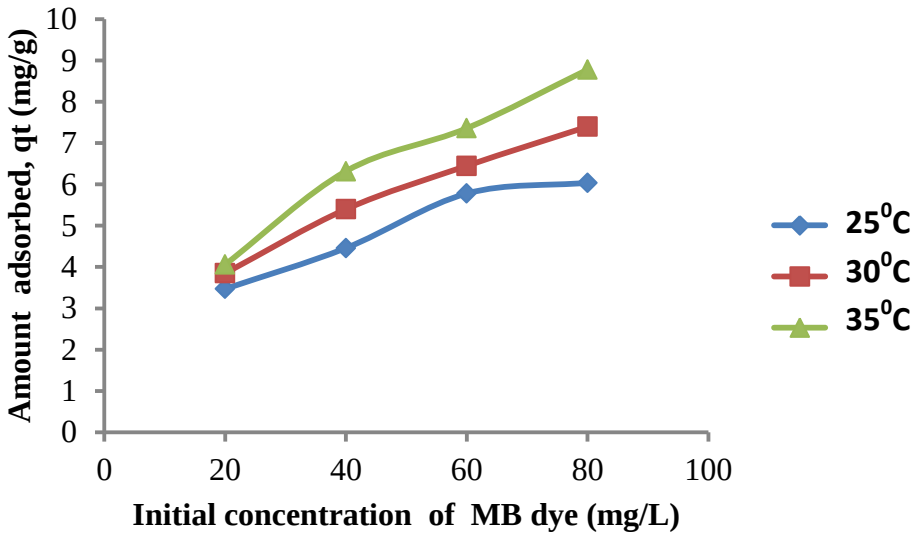


Figure 7.Plot of amount adsorbed versus initial concentration of MB dye on CHACatpH = 11.

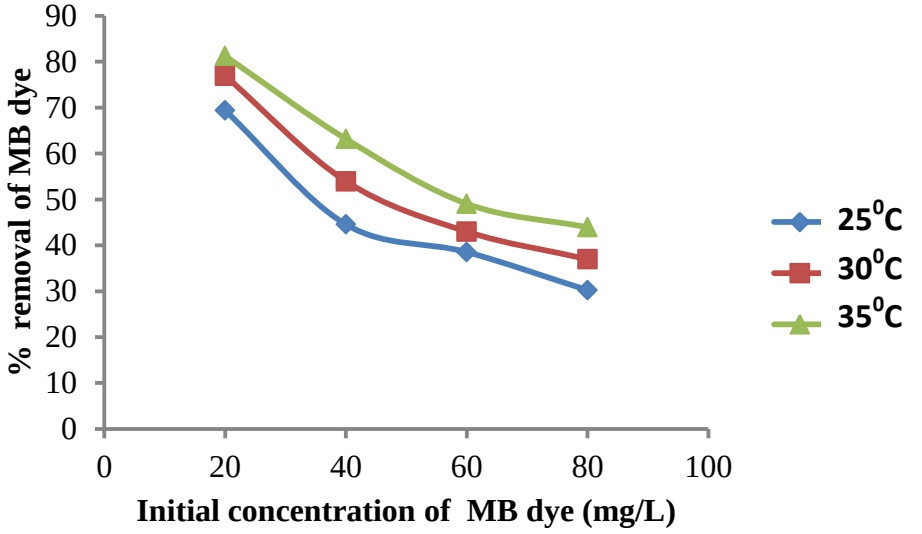


Figure8.Plot of percent removal of MB dye versus initial concentration of the dye by CHAC at pH = 11.

4.2.1.4. **Contact time**

The results of adsorption of MB dye on CHAC are presented in Figures 9,(Plot of percent removal of MB dye on CHAC versus contact time at pH = 11, adsorbent dosage = 0.2 g/50 mL of MB solution, agitation speed = 250 rpm, particle size < 250 µm, and temperature = 24 $\pm$ 1$^{o}$C). and Figures 10(Plot of amount of MB adsorbed on CHAC versus contact time at pH = 11, adsorbent dosage = 0.2 g/50 mL of MB solution, agitation speed = 250 rpm, particle size < 250 µm, and temperature = 24 $\pm$ 1$^{o}$C. The adsorption capacity and removal of dye initial concentration were rapid at the initial stages and becomes slow in later stages till saturation is attained. The final dye concentration did not vary significantly after 60 min from the start of adsorption process. The time beyond no significant change in adsorption takes place has been fixed as equilibrium time. This shows that equilibrium can be assumed at 60 min since the value of $\log(q_e - q_t) = 0$ (Appendix Table 7). The adsorption capacity at equilibrium increases from 4.795 to 8.338 mg/g whereas the percentage removal of dye decreased from 95.90 to 41.69% with an increase in initial MB concentration from 20 to 80 mg/L (Appendix Table 7). The adsorption capacity and rate of percent removal are higher at the beginning due to larger surface area of the adsorbent available for the adsorption of dye more quickly at low concentration and later case the available adsorption sites are saturated and unable to accommodate the higher concentration of the adsorbate (Poots. VJP., 1976). During the experiment was carried out, a great color reduction was observed at contact time of 60 min to achieve equilibrium

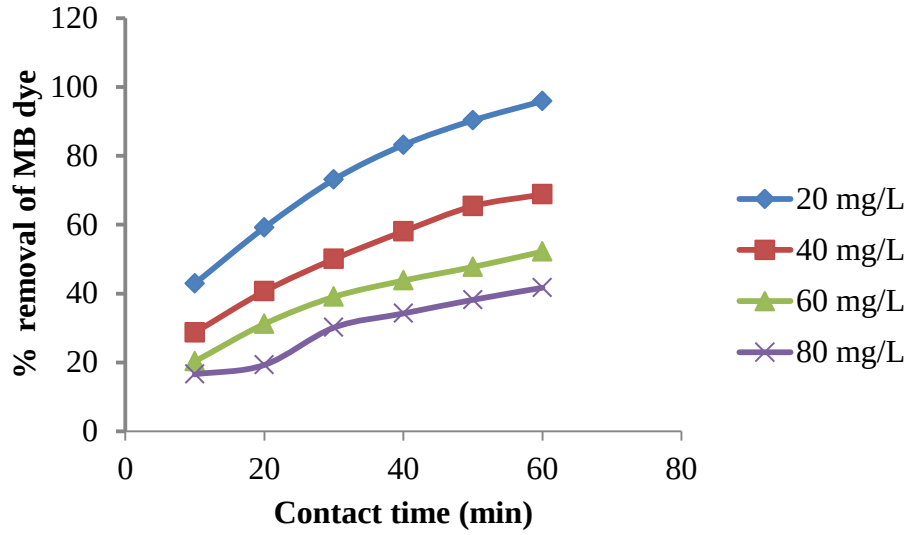


Figure 9. Plot of percent removal of MB dye on CHAC versus contact timeat pH = 11.

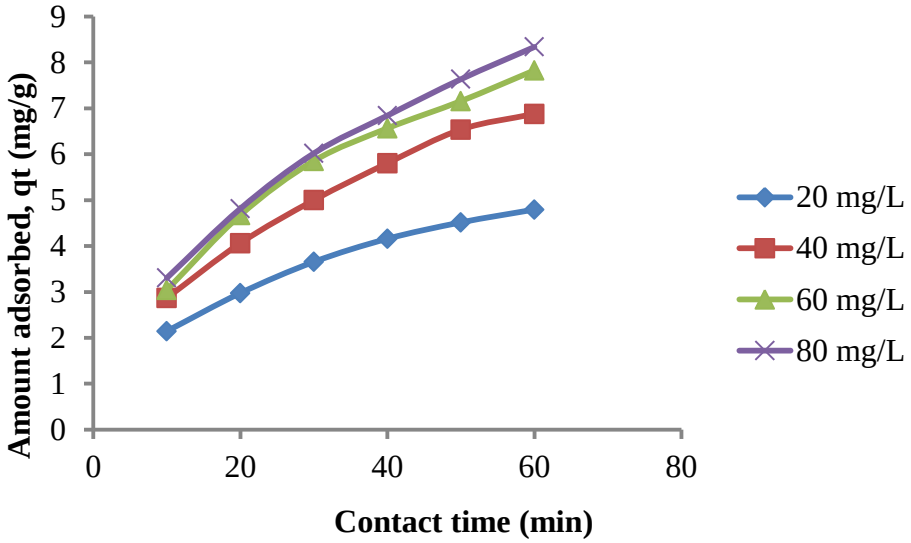


Figure 10. Plot of amount of MB adsorbed on CHAC versus contact time at pH = 11.

### 4.3. Kinetic Studies

#### 4.3.1. **Pseudo-first order kinetic model**

Lagergren's kinetic equation describes the adsorption of liquid-solid systems based on solid capacity. In order to distinguish kinetic equations based on concentration of solution and adsorption of a solid, Lagergren's first-order rate equation was applied (Shahryari, 2010).

A plot of log ($q_e$-$q_t$) versus t described in the literature part (section 2.5.3.1 equation 9) gives a linear line curve as shown in Figure 11 (Plot of pseudo-first-order adsorption of MB on CHAC. at initial concentrations of 20, 40, 60 and 80 mg/L, adsorbent dosage = 0.2 g/50 mL of MB solution, contact time 60 min, pH = 11, temperature = 24±1°C, agitation speed = 250 rpm, and particle size < 250µm). From this curve the values of $k_1$ and $q_{e1}$ were determined using the slope and intercept of the line, respectively and these values are presented on Table 4. As it can be observed from Table 4, the $k_1$ and $q_{e1}$ values for pseudo-first-order model vary between 5.537x$10^{-2}$to 4.606x$10^{-2}$$min^{-1}$and 5.248 to 8.933 mg/g, respectively.

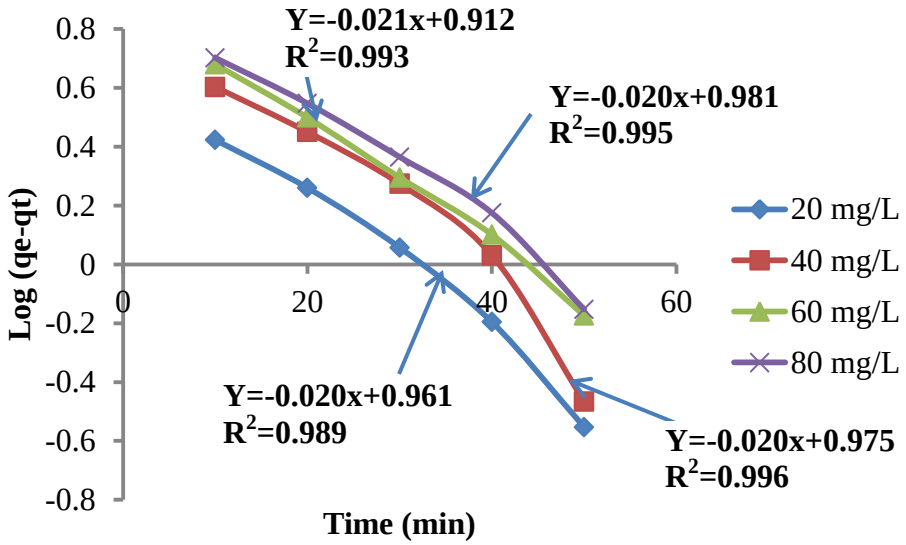


Figure 11.Plot of pseudo-first-order adsorption of MB on CHAC.

4.3.2. **Pseudo-second-order kinetic model**

The pseudo-second-order adsorption rate equation usually considers the adsorption capabilities of solids. A plot of $t/q_t$ versus t described in literature (section 2.5.3.2 equation 11) gives a linear relationship as depicted in Figure 12(Plot of pseudo-second-order kinetic model adsorption of MB on CHAC at initial concentrations of 20, 40, 60, and 80 mg/L, adsorbent dosage = 0.2 g/50mL of MB solution, contact time = 60 min, agitation speed = 250 rpm, particle size < 250µm, pH = 11 and temperature = 24$\pm$1$^{o}$C).

Accordingly the values of $q_{e2}$ and $K_2$ were determined similarly from the slope and intercept of the plot, respectively and the values obtained as such are presented in Table 4. The experimental data were analyzed and the predicted values from both models are compared based on the respective $R^2$ values. A relative high $R^2$ value indicates that the model successfully describes the kinetics of adsorption of an adsorbate on a given adsorbent.

Accordingly, it can be inferred from the $R^2$ values of the two models, such that the adsorption of MB on CHAC may be more favorable by the pseudo-second-order kinetic model than it could be so by pseudo-first-order model. It then follows to suggest that the adsorption process in this particular study can be approximated more favorably by the pseudo-second-order kinetic model. This further suggests that the adsorption process is of a chemisorption type that would possibly involve exchange or sharing of electrons between the adsorbent and adsorbate (Namasivayam, 2002) (Chandra, 2007). The equilibrium adsorption capacity, $q_{e2}$, increased from 6.579 to 12.195 mg/g when the initial concentration of the dye has increased from 20 to 80 mg/L (Table 4).This is indicative of the fact that the dye removal is highly dependent on dye initial concentration. While the initial concentration varies from 20 to 80 mg/L, the rate constant $K_2$ decreases from $6.740x10^{-3}$ to $2.799x10^{-3}$ g/mg.min. Similar results reported on the adsorption of MB onto dehydrated wheat bran carbon (Dursum, 2007) and carbon nanotubes (Shahryari, 2010)

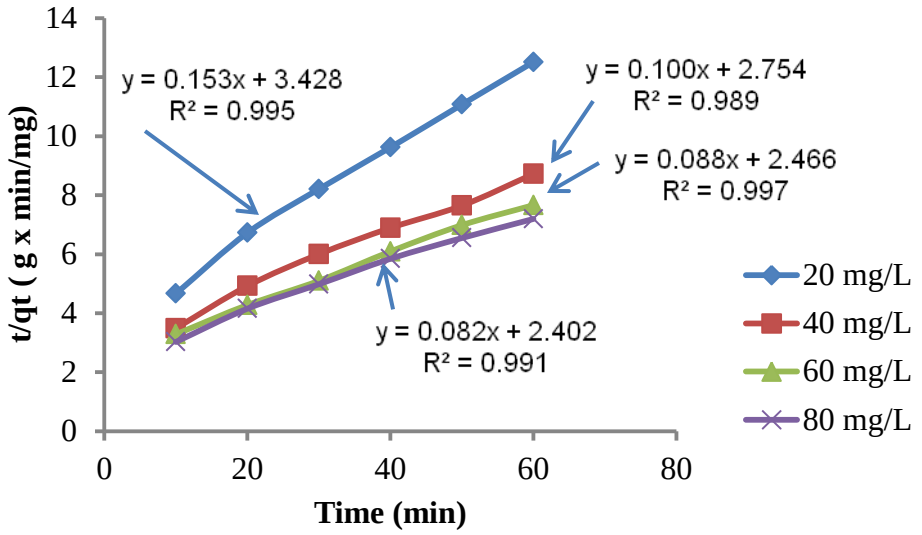


Figure 12 Plot of pseudo-second-order kinetic model adsorption of MB on CHAC.

### 4.3.3. **Intra-particle diffusion**

In order to gain idea of adsorption mechanism and to determine whether intra-particle diffusion is the rate limiting step or not the kinetic experimental results were fitted to the Weber's intra-particle diffusion (Weber, 1963). A plot of $q_t$ versus $t^{1/2}$ described in the literature part (section 2.5.3.3 equation 12)and as shown in Figure 13 from which the values of intra-particle diffusion rate constant '$K_i$' intersects 'C' and $R^2$as determined at different dye initial concentrations (see results in Table 4). If a plot of $q_t$ versus $t^{1/2}$is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step (Rauf, 2008). From Figure 13(Plot of intra-particle diffusion of MB on CHAC at initial concentrations of 20, 40, 60, and 80 mg/L, adsorbent dosage = 0.2 g/50mL of MB solution, contact time = 60min, agitation speed = 250 rpm, particle size < 250µm, pH = 11 and temperature = 24±1$^{o}$C).It can be noted that the linear plots did not pass through the origin for each concentration level. This indicates that although intra-particle diffusion was involved in the adsorption process, it was not the sole rate-limiting step. This also confirms that adsorption of MB on the adsorbent was a multi-step process involving adsorption on the external surface as well as diffusion into the interior (Bhattacharyya and Sharma, 2005). Intra-particle diffusion rate constant '$K_i$' increases with increase in dye initial concentration (Table 4). The increase in diffusion rate constant at higher dye initial concentration may be attributed to larger adsorbate concentration gradient between the surface and the bulk solution

(Yadav, 2011); (Sarita, 2011)). On the other hand, the intercept of the plot reflects the boundary layer effect. The larger intercept indicates the greater contribution of the surface adsorption in the rate limiting step.

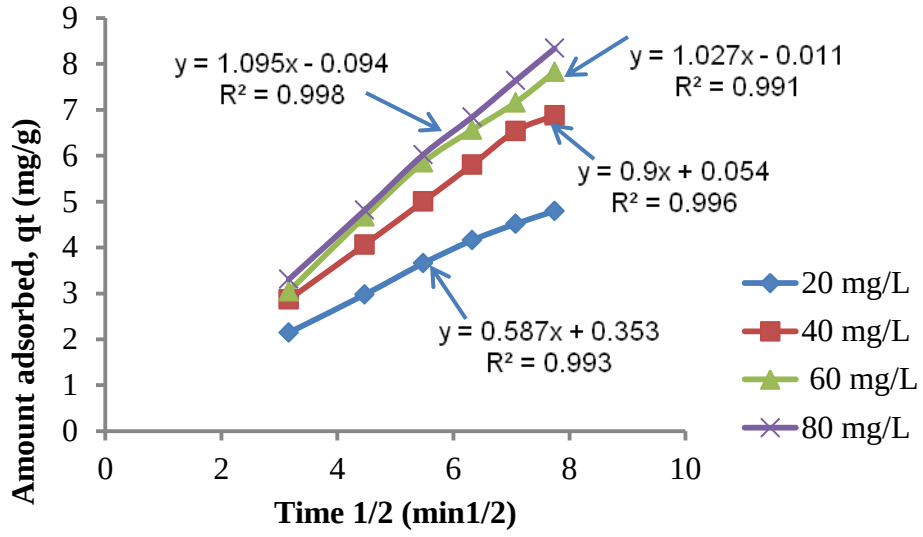


Figure 13.Plot of intra-particle diffusion of MB on CHAC.

Table 4. Shows the kinetic adsorption of pseudo-first-order, pseudo-second-order and intra-particle diffusion rate constants.

| $C_o$(mg/g) | Pseudo-1st-order | | | Pseudo-2nd-order | | | Intra-particle diffusion model | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_{e1cal(mg/g)}$ | $K_1$ | $R^2$ | $q_{e2cal(mg/g)}$ | $K_2$ | $R^2$ | $K_i$ | C | $R^2$ |
| 20.0 | 5.25 | 5.54 | 0.98 | 6.58 | 6.74 | 0.99 | 0.59 | 0.35 | 0.93 |
| 40.0 | 8.11 | 5.76 | 0.93 | 10.00 | 3.63 | 0.99 | 0.90 | 0.05 | 0.99 |
| 60.0 | 8.17 | 4.84 | 0.99 | 11.36 | 3.14 | 0.99 | 1.03 | -0.01 | 0.99 |
| 80.0 | 8.93 | 4.61 | 0.98 | 12.19 | 2.80 | 0.99 | 1.09 | -0.09 | 0.99 |

### 4.4.Mechanism of Adsorption

Adsorption of solute from aqueous solutions on to adsorbent (AC) may be caused by a high affinity of the solute for the carbon. Many adsorptions of organic substances by AC result from specific interactions between functional groups on the adsorbate and on the surface of the adsorbent. Lower adsorption of MB was observed on CHAC at pH = 2, but its value has increased with the increasing initial pH of the dye solution from 2 to 11.This trend may suggest that the carbon surface being negatively charged, it favors adsorption of the cationic dye on its

available sites. Therefore, the adsorption of this charged dye on the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the pH of the solution.

The $pH_{pzc}$ value for CHAC was 6.52. At pH values below $pH_{pzc}$ the adsorbent has a net positive charge which results in electrostatic repulsion between the surface of AC and the MB dye, because MB is a cationic dye denoted by the presence of a positive charge on nitrogen in its structure. At pH values greater than $pH_{pzc}$ the adsorbent has a net negative charge which results in electrostatic attraction between the surface of AC and MB dye. The potential of carbon surface in aqueous solution is determined by the activity of $H^+$ and $OH^-$ ions which can be bonded with the carbon surface forming complex ions.

At low pH the reaction might be:

$$\text{Carbon-OH} + H^+ \longrightarrow \text{Carbon-}OH_2^+ \quad (16)$$

$$\text{Carbon-}OH_2^+ + \text{Dye}^+ \longrightarrow \text{Carbon-O (Dye}^+\text{)} + 2H^+ \quad (17)$$

At high pH the reaction might be:

$$\text{Carbon-OH} + OH^- \longrightarrow \text{Carbon-}O^- + H_2O \quad (18)$$

$$\text{Carbon-}O^- + \text{Dye}^+ \longrightarrow \text{Carbon-O (Dye)} \quad (19)$$

A similar theory was proposed by some researchers for adsorption of MB onto a low cost natural Jordanian Tripoli (Alzaydien, 2009) and adsorption of malachite green onto acid activated low cost carbon (Venkatraman, 2011).

# 5. CONCLUSION AND RECOMMENDATIONS

## 5.1. Conclusions

In the present work CHAC was used as an adsorbent to study its removal efficiency towards MB dye from aqueous solutions by adsorption.. Adsorption of MB on CHAC obeys both the Langmuir and Freundlich isotherms. The equilibrium data were found to fit well with the Langmuir adsorption isotherm. This indicates the homogeneous distribution of active sites on the adsorbent surface. The maximum adsorption capacity '$Q_e$' and adsorption energy 'b' were found to be 8.55 mg/g and 0.55 L/mg, respectively from the Langmuir adsorption model. Values of the equilibrium parameter '$R_L$' from Langmuir isotherm range between 0.022-0.083 and values of adsorption capacity '$K_f$' and adsorption intensity 'n' from the Freundlich isotherm were 4.91 mg/g and 7.30,respectively, indicating that the adsorption process of MB dye on prepared adsorbent is favorable. Comparison of the adsorption capacity '$Q_e$' of the adsorbent with the data in the literature reveals that CHAC had adsorption capacity 8.55 mg/g. Effects of various parameters such as dye initial concentration, pH, temperature and contact time were studied. The equilibrium adsorption occurred at 60 min, temperature of ($24\pm1^oC$) and pH =11. The amount adsorbed and the removal of MB dye from the solution increases rapidly at the initial stage and slows down towards equilibrium time. The percentage removal of MB dye decreases as the dye initial concentration increases. However, the amount of dye adsorbed increases with increase in dye initial concentration. The results of pH effect reveal that minimum adsorption occurred at pH = 2 and maximum at pH = 11. The workable pH for the removal of MB was found to be between 6 and 11. The percentage removal of MB increases as the pH of the solution increases. The temperature result reveals that the percentage removal of dye adsorbed increases with increase in temperature. Kinetic studies have been carried out by assuming each of the pseudo-first-order, pseudo-second-order and intra-particle diffusion mechanisms.

The data obtained however indicate that the adsorption kinetics follow better the pseudo-second-order model and intra-particle diffusion is also the rate determining step. The rate constant for pseudo-first-order is $5.537x10^{-2}$, $5.758x10^{-2}$,$4.836x10^{-2}$ and, $4.606x10^{-2}$ $min^{-1}$ and intra-particle diffusion coefficient is 0.587, 0.900, 1.027, and 1.095 $mg/g.min^{1/2}$ for dye initial concentration of 20, 40, 60,and 80 mg/L.

### 5.2. Recommendations

1. As this research is the study on dye removal from colored wastewater by using activated carbon, further work should be carried out on effluents and its catchment by considering environmental matrices such as water, biota, and plants.
2. At the same time enhancing awareness of the community should be done on the possible effects (impacts) of river water containing dyes.
3. Initiating systematic researches in which expertise of varied skills could participate may also help in order to come-up with a sustainable solution, where the results of the current finding could also be employed in some integrated manner
4. Further study on the applicability of the adsorbent to the real situation where large volume of waste effluent is being discharged is also mandatory.

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# 7. APPENDICES

## 7.1. Appendix Table

Table 1. Values for Langmuir and Freundlich adsorption plot

| $C_o$(mg/g) | $C_e$(mg/L) | $q_e$(mg/g) | $C_e/q_e$(g/L) | log$C_e$(mg/L) | log$q_e$(mg/g) |
|---|---|---|---|---|---|
| 20.0 | 0.82 | 4.79 | 0.17 | -0.09 | 0.68 |
| 40.0 | 12.48 | 6.88 | 1.81 | 1.09 | 0.84 |
| 60.0 | 28.69 | 7.82 | 3.66 | 1.46 | 0.89 |
| 80.0 | 46.65 | 8.33 | 5.59 | 1.67 | 0.92 |

$C_o$ = Initial concentration of MB dye, $C_e$ = Equilibrium concentration of MB dye, $q_e$ = Amount of MB dye adsorbed at equilibrium concentration.

Table 2.Dimensionless Separation factor, $R_L$ at room temperature ($24\pm1^oC$) for adsorption of MB on CHAC.

| Initial concentration, $C_o$ of MB dye (mg/L) | $R_L$ |
|---|---|
| | b =0.55 |
| 20.0 | 0.08 |
| 40.0 | 0.04 |
| 60.0 | 0.03 |
| 80.0 | 0.02 |

Table 3. Values of pH initial, pH final and pH final-pH initial of CHAC for point of zero charge determination.

| pH initial | pH final | pH final-pH initial |
|---|---|---|
| 11 | 7.63 | -3.37 |
| 10 | 7.21 | -2.77 |
| 9 | 6.96 | -2.04 |
| 8 | 6.61 | -1.39 |
| 7 | 6.57 | -0.43 |
| 6 | 6.49 | 0.49 |
| 5 | 5.66 | 0.66 |
| 4 | 4.62 | 0.62 |
| 3 | 3.54 | 0.54 |
| 2 | 2.92 | 0.92 |

Table 4. Effect of pH on adsorption of MB on CHAC at initial concentration of 20 mg/L, adsorbent dosage = 0.2 g/50 mL of MB solution, contact time 30 min, agitation speed 250 rpm, particle size < 250 μm and temperature =24$\pm$ 1$^{o}$C

| pH | Final conc. of MB dye,$C_t$ (mg/L) | Amount of MB dye adsorbed, $q_t$(mg/g) | % removal of MB dye |
|---|---|---|---|
| 2.0 | 15.02 | 1.25 | 24.90 |
| 3.0 | 9.87 | 2.55 | 50.65 |
| 4.0 | 7.85 | 3.09 | 60.75 |
| 5.0 | 6.95 | 3.26 | 65.25 |
| 6.0 | 5.06 | 3.74 | 74.70 |
| 7.0 | 4.95 | 3.76 | 75.25 |
| 8.0 | 2.30 | 4.43 | 88.50 |
| 9.0 | 1.61 | 4.59 | 87.45 |
| 10.0 | 1.23 | 4.69 | 91.95 |
| 11.0 | 0.51 | 4.87 | 97.95 |

Table 5. Effects of dye initial concentration of MB on CHAC at pH =11, adsorbent dosage = 0.2 g/50 mL of MB solution, contact time = 30 min, agitation speed = 250 rpm, particle size < 250 µm and temperature = 24±1$^{o}$C.

| Initial conc. of MB dye $C_o$ (mg/L) | Final conc. of MB dye, $C_t$(mg/L) | Amount of MB dye adsorbed, $q_t$ (mg/g) | % removal of MB dye |
|---|---|---|---|
| 20.0 | 6.26 | 3.44 | 68.70 |
| 40.0 | 21.82 | 4.55 | 45.45 |
| 60.0 | 37.07 | 5.73 | 38.22 |
| 80.0 | 55.37 | 6.16 | 30.79 |

Table 6. Effect of temperature on adsorption of MB on CHAC at initial concentrations of 20, 40, 60, and 80 mg/L, adsorbent dose = 0.2g/50 mL of MB solution, contact time 30 min, agitation speed =250 rpm, particle size < 250µm and pH =11.

| Initial conc$C_o$( mg/L | Final conc. of MB dye, $C_t$(mg/L) | | | Amount of MB dye adsorbed, $q_t$ (mg/g) | | | % removal of MB dye | | |
|---|---|---|---|---|---|---|---|---|---|
| | Temperature ($^{o}$C) | | | | | | | | |
| | 25 | 30 | 35 | 25 | 30 | 35 | 25 | 30 | 35 |
| 20.0 | 6.12 | 4.61 | 3.75 | 3.47 | 3.85 | 4.06 | 69.40 | 76.95 | 81.25 |
| 40.0 | 22.18 | 18.42 | 14.73 | 4.46 | 5.40 | 6.32 | 44.55 | 53.95 | 63.18 |
| 60.0 | 36.88 | 34.21 | 30.57 | 5.78 | 6.45 | 7.36 | 38.53 | 42.99 | 49.05 |
| 80.0 | 55.83 | 50.42 | 44.87 | 6.04 | 7.40 | 8.78 | 30.22 | 36.98 | 43.94 |

Table 7. The value of kinetic parameters of adsorption of MB on CHAC and experimental data at initial concentrations of 20, 40, 60, and 80 mg/L, adsorbent dose =0.2 g/50mL of MB solution, contact time 60 min, agitation speed =250 rpm, particle size <250 µm, pH = 11 and temperature =27± 1°C.

| Time (min) | $C_o$ (mg/L) | $C_t$(mg/L) | $q_e$(mg/g) | $q_t$(mg/g) | Log($q_e$-$q_t$) | $t/q_t$ | % removal |
|---|---|---|---|---|---|---|---|
| 10 | 20 | 11.42 | 4.79 | 2.15 | 0.42 | 4.66 | 42.90 |
| | 40 | 28.53 | 6.88 | 2.87 | 0.60 | 3.49 | 28.68 |
| | 60 | 47.83 | 7.83 | 3.04 | 0.68 | 3.29 | 20.28 |
| | 80 | 66.78 | 8.34 | 3.31 | 0.70 | 3.03 | 16.53 |
| 20 | 20 | 8.17 | 4.79 | 2.98 | 0.26 | 6.72 | 59.15 |
| | 40 | 23.75 | 6.88 | 4.06 | 0.45 | 4.92 | 40.63 |
| | 60 | 41.30 | 7.83 | 4.68 | 0.49 | 4.28 | 31.17 |
| | 80 | 60.74 | 8.34 | 4.82 | 0.55 | 4.15 | 19.26 |
| 30 | 20 | 5.38 | 4.79 | 3.66 | 0.06 | 8.21 | 73.10 |
| | 40 | 20.00 | 6.88 | 5.00 | 0.27 | 6.00 | 50.00 |
| | 60 | 36.58 | 7.83 | 5.86 | 0.29 | 5.09 | 39.03 |
| | 80 | 55.92 | 8.34 | 6.02 | 0.37 | 4.98 | 30.10 |
| 40 | 20 | 3.37 | 4.79 | 4.16 | -0.19 | 9.62 | 83.15 |
| | 40 | 16.78 | 6.88 | 5.81 | 0.03 | 6.89 | 58.05 |
| | 60 | 33.74 | 7.83 | 6.57 | 0.10 | 6.09 | 43.77 |
| | 80 | 52.63 | 8.34 | 6.84 | 0.18 | 5.85 | 34.21 |
| 50 | 20 | 1.94 | 4.79 | 4.52 | -0.55 | 11.07 | 90.30 |
| | 40 | 13.85 | 6.88 | 6.54 | -0.47 | 7.65 | 65.38 |
| | 60 | 31.37 | 7.83 | 7.16 | -0.17 | 6.99 | 47.72 |
| | 80 | 49.46 | 8.34 | 7.64 | -0.15 | 6.55 | 38.18 |
| 60 | 20 | 0.82 | 4.79 | 4.79 | - | 12.51 | 95.90 |
| | 40 | 12.48 | 6.88 | 6.88 | - | 8.72 | 68.80 |
| | 60 | 28.69 | 7.83 | 7.83 | - | 7.66 | 52.18 |
| | 80 | 46.65 | 8.34 | 8.34 | - | 7.19 | 41.69 |

## 7.2. Appendix Figure

Figure 1. Calibration curve of MB dye for different initial concentrations at 663 nm.