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Republic of Iraq
Ministry of Higher
Education and
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University of Babylon
College of Engineering
Dept. of Civil Engineering

EVALUATION OF METHYLENE BLUE REMOVAL FROM WASTEWATER BY ADSORPTION ONTO DIFFERENT TYPES OF ADSORBENT BEDS

A Thesis

Submitted to the College of Engineering
of the University of Babylon in Partial
Fulfillment of the Requirements
for the Degree of Master
in Environmental
Engineering

By

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March / 2009

Rabeea Al-Awal 1430 H

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Wissam Altaliby
2009

ABSTRACT

The aim of this research is to evaluate the applicability of using locally available materials and commercial activated carbon for the adsorption of methylene blue dye using continuous system (fixed bed).

Two local materials in addition to commercial activated carbon, were evaluated for the adsorption process. These materials included Iraqi porcellanite rocks and activated carbon prepared from Iraqi palm-date pits.

Seventeen experiments and different column systems were carried out at various adsorbent types, initial concentrations, flow rate, bed depth, and different weight ratios of date pits AC-commercial AC and porcellanite-commercial AC. Two types of experiments were carried out, batch experiments and continuous flow (column system) experiments. Batch study showed that equilibrium isotherms for all the adsorbents used in the study are of favorable type. The equilibrium data for methylene blue adsorption on different adsorbents well fitted to the Langmuir equation, with maximum monolayer adsorption capacities of (23.09 mg/g), (22.42 mg/g), and (14.88 mg/g) exhibited by porcellanite, commercial activated carbon and the produced activated carbon respectively. Porcellanite achieved higher removal efficiencies followed by commercial activated carbon and date-pits activated carbon. Column experiments (continuous system) showed that the use of granular porcellanite instead of GAC reduces the operating time by only about 11% at similar operation conditions. While the use of the produced date-pits activated carbon reduces the operating time by about 35% compared to GAC at similar operation conditions.

It was found that adding 10%, 12% and 15% porcellanite weight ratios to the activated carbon bed increases the operating time by about 18%, 28% and 30% respectively, while adding 30% porcellanite weight ratio causes the operating time to decrease as compared to 10%, 12% and 15% ratios, but the bed was still achieving slightly higher operating time and removal efficiency than the pure (0% ratio) carbon bed.

Adding 10% and 12% date-pits activated carbon to the commercial activated carbon bed increases the operating time of the bed by about 10% and 22% respectively. It can be seen also that increasing the date-pits ratio to 15% and 17% reduces the operating time by about 5% and 28% respectively and therefore makes the adsorption process not efficient as compared with 0% date-pits ratio.

(Data Fit version 9.0) program was used for the statistical analysis of the experimental results by developing a multiple regression model between the dependent variable (operating time, t) and the independent variables, flow rate (Q), initial concentration (Co), bed depth (L), date pits ratio (DP), and porcellanite ratio (P). The coefficient of determination (R^2) of (0.95) for the obtained model illustrates that the experimental data correlated well with the modeling data.

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CHAPTER FOUR

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Nomenclature

Symbol	Definition	Unit
1/n	Freundlich equation parameter	(m^3/kg)
b	Langmuir equation parameter	(m^3/kg)
C_e	Dye concentration at equilibrium	(ppm)
C_o	Initial concentration of dye	(ppm)
C_t	Dye concentration at given time	(ppm)
DP	Date-pits Activated Carbon Ratio	%
GAC	Granular Activated Carbon	
K	Freundlich equilibrium parameter	(kg/kg)
L	Bed depth of adsorbent	(m)
MTZ	Mass transfer zone	
P	Porcellanite Ratio	%
PAC	Powdered Activated Carbon	
q	Adsorption ratio at given time	**kg/kg** of carbon
Q	Flow rate	(m^3/sec)
q_e	Adsorption ratio at equilibrium	kg/kg
Q_o	Langmuir equation parameter	(kg/kg)
R^2	Coefficient of Determination	
R_L	Dimensionless equilibrium parameter	
t	Time	(min)
T	Temperature	(k)
V	Solution volume	(liter)

W	Mass of the adsorbent	mg
X	Mass of adsorbate	(kg)
λ_{max}	Wavelength at which max. absorbency of MB occurs	nm

بسم الله الرحمن الرحيم

ونزلنا من السماء ماء مباركا فأنبتنا به جنات
وحب الحصيد ۞ والنخل باسقات لها طلع
نضيد ۞ رزقا للعباد وأحيينا به بلدة ميتا
كذلك الخروج ۞

صدق الله العظيم

من سورة ق

الآيات من ٩ إلى ١١

الخلاصة

الهدف من هذا البحث هو تقييم مدى إمكانية استخدام مواد متوفرة محليا وكذلك الكربون المنشط التجاري لغرض إمتزاز صبغة المثيلين الزرقاء باستخدام طريقة النمط المستمر (الطبقة الساكنة) ، وقد تم تقييم أداء مادتين محليتين بالإضافة إلى الكربون المنشط التجاري في عملية الامتزاز وهما كل من صخور البورسيلانايت العراقية والكربون المنشط المنتج من نوى التمر العراقي.

تم إجراء سبعه عشرة تجربة من تجارب النمط المستمر (continuous system) لدراسة مدى تأثر عملية الامتزاز بكل من نوع المادة ألمازة ، التركيز الأولي للمادة الممتزة ، معدل الجريان ، ارتفاع الحشوة ، وكذلك لدراسة مدى تأثر عملية الامتزاز باستخدام نسب وزنيه مختلفة من مادة البورسيلانايت-الكربون المنشط التجاري واستخدام نسب من الكربون النشط المنتج من النوى-الكربون المنشط التجاري.

تم خلال الدراسة الحالية إجراء نوعين من التجارب تضمنت تجارب دفعية (batch) وتجارب النمط المستمر(continuous system). وقد أظهرت التجارب الدفعية أن علاقة التوازن لكل من المواد ألمازة الثلاثة المستخدمة في البحث هي من النوع المفضل (favorable type). كما أظهرت هذه التجارب أن علاقة التوازن لامتزاز صبغة المثيلين الزرقاء على المواد المازة الثلاثة تتطابق جيدا مع نموذج لانكمير وقد كانت قيم سعة الامتزاز القصوى بمقدار (23.09 ملغم/غ) ، (22.42 ملغم/غ) ، و (14.88 ملغم/غ) لكل من البورسيلانايت ، الكربون المنشط التجاري و الكربون المنتج من النوى على التوالي. حيث تبين أن البورسيلانايت اظهر أعلى كفاءة امتزاز يتبعه الكربون التجاري وبفارق بسيط جدا وأخيرا الكربون المنتج من النوى.

أما تجارب النمط المستمر فقد بينت أن استخدام البورسيلانايت الحبيبي بدلا من الكربون المنشط التجاري في عمود الامتزاز يؤدي إلى تقليل زمن التشغيل لعمود الامتزاز بنسبة حوالي 11% فقط عند نفس ظروف التشغيل. بينما استخدام الكربون المنتج من النوى بدلا من الكربون المنشط التجاري في عمود الامتزاز فيؤدي إلى تقليل زمن تشغيل العمود بنسبة حوالي 35 % عند نفس ظروف التشغيل.

وجد أن إضافة نسب وزنيه مختلفة (10 % ، 12 % ، 15 %) من مادة البورسيلانايت إلى عمود الحشو الثابت للكربون يؤدي إلى زيادة زمن التشغيل لعمود الامتزاز بنسبة حوالي (18 % ، 28 % ، و 30 %) على التوالي. أما إضافة 30 % من البورسيلانايت كنسبة وزنية

إلى عمود الحشو فيسبب نقصان زمن تشغيل العمود ليصبح اقل مما كان عليه عند إضافة النسب (10 % ، 12 % ، 15 %) ، إلا أن عمود الحشو في هذه الحالة بقي يعمل بكفاءة امتزاز وزمن تشغيل أعلى بقليل منه في حالة استخدام الكربون التجاري بمفرده وبدون إضافة البورسيلانايت.

إن إضافة نسب وزنيه مختلفة (10 % و 12 %) من الكربون المنشط المنتج من النوى إلى عمود الحشو الثابت للكربون التجاري يسبب زيادة زمن التشغيل لعمود الامتزاز بنسبة حوالي 10 % و 22 % على التوالي. وفي حالة زيادة النسبة المضافة من الكربون المنتج إلى 15 % و 17 % فان ذلك يؤدي إلى تقليل زمن التشغيل بنسبة حوالي 5 % و 28 % على التوالي ، وهذا ما يجعل عملية الامتزاز غير كفوءة بالمقارنة مع استخدام الكربون المنشط التجاري بمفرده.

تم استخدام البرنامج الإحصائي (Data Fit version 9.0) لإجراء عملية التحليل الإحصائي للنتائج التجريبية وبناء موديل رياضي من المتغيرات المستقلة (نسبة الكربون المنتج من النوى، عمق طبقة الكربون، التركيز الابتدائي لصبغة المثيلين، معدل الجريان و نسبة البورسيلانايت) والمتغير المعتمد (زمن التشغيل، t) ، وقد وجد أن النتائج التجريبية تتطابق بشكل جيد مع هذا الموديل الرياضي.

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Appendix A

UV Spectrophotometer Calibration Curves

A: Absorbency – Concentration Relationship

A calibration curve for the UV instrument was constructed for MB concentrations versus absorbency at 664 nm wavelength as shown in fig.(A.1).

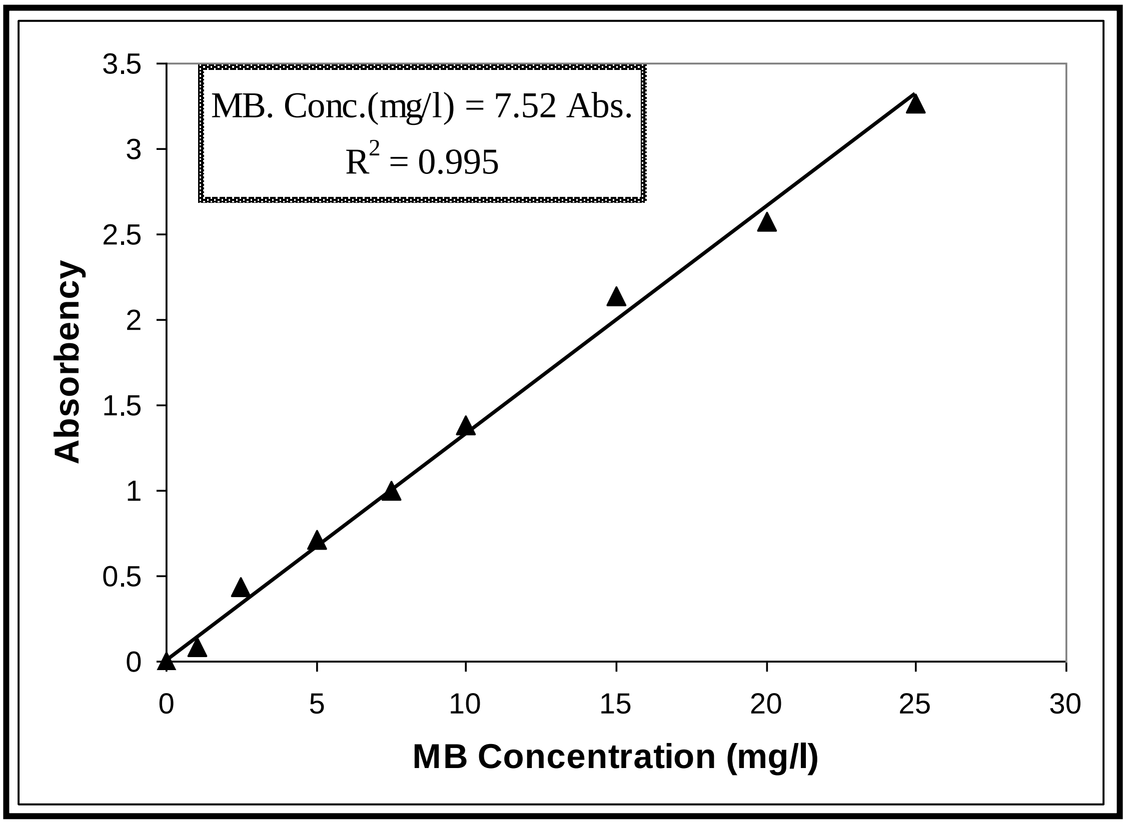


Fig.(A.1) UV. Spectrophotometer Calibration Curve

B: Maximum Wavelength (λ_{max}) Determination Result

λ_{max} is the wavelength at which maximum MB absorbency occurs. It is determined by performing a scan on a MB solution sample by the spectrophotometer. The scan result chart is given in fig.(A.2).

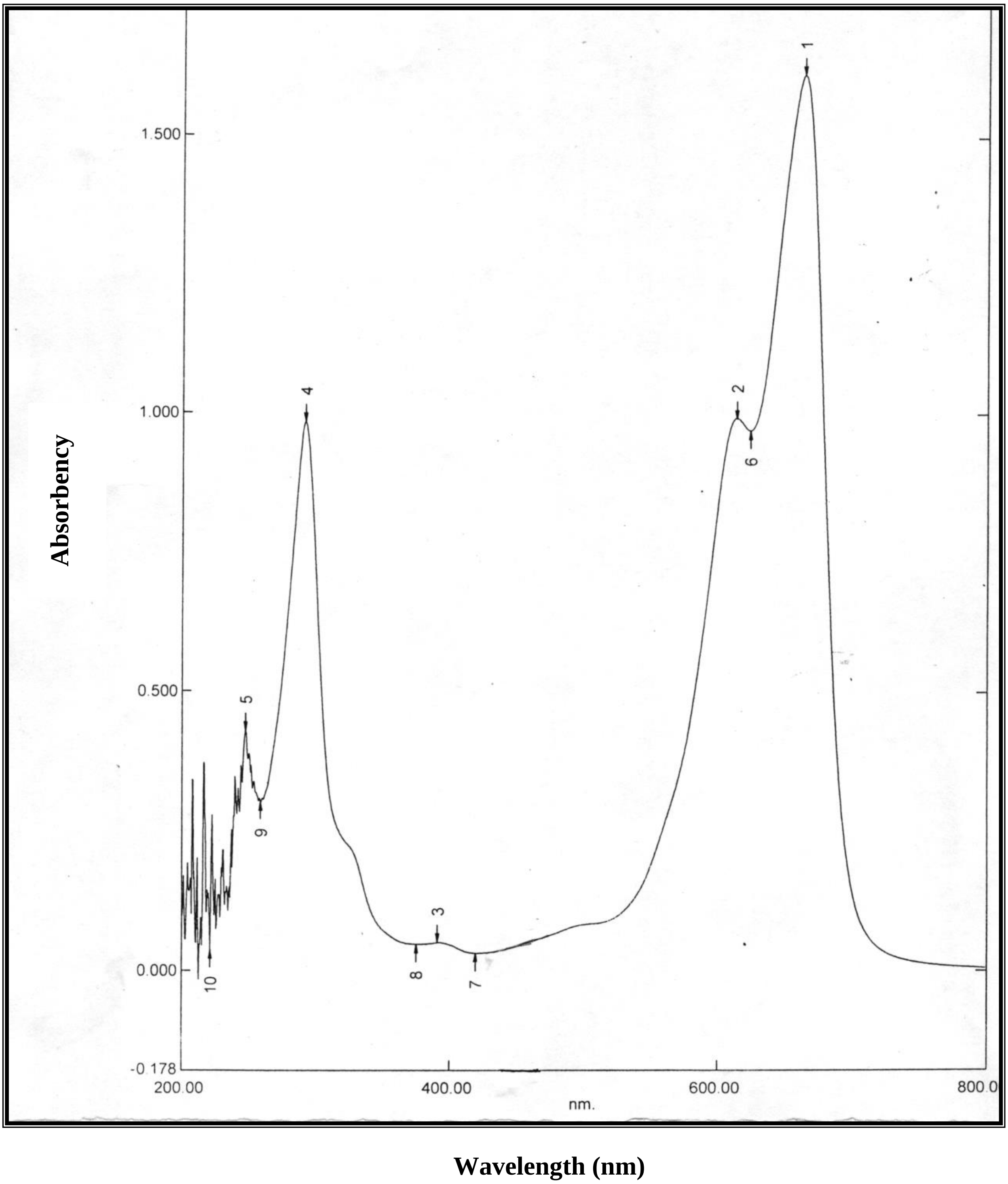


Fig.(A.2) Scan chart of UV. Spectrophotometer

Appendix B

Sample of Calculations

Calculation of the amount of MB dye adsorbed at equilibrium

The amount of MB dye adsorbed at equilibrium, q_e (mg/g), was calculated by the following equation:

$$q_e = \frac{(C_O - C_e)V}{W}$$

Where:

q_e: the amount of methylene blue dye adsorbed at equilibrium (mg/g)

C_O: the initial dye concentration (mg/l)

C_e: the equilibrium dye concentration (mg/l)

V: the volume of the dye solution (liter)

W: the mass of dry adsorbent used (g)

For example, for MB adsorption onto porcellanite at the following conditions:

C_O= 100 mg/l, C_e= 2.7978 mg/l, V= 0.1 liter, and W= 0.6 mg:

The value of (q) was calculated by using the above equation and it was 16.2 mg/g.

CHAPTER ONE

INTRODUCTION

1.1 Background

Dyes are widely used in textile, paper, plastic, food and cosmetic industries. The wastes coming from these industries can affect our atmosphere causing pollution. The level of pollutants even at a very low concentration is highly visible and it affects aquatic life as well as food web. Many dyes are difficult to degrade. They are generally stable to light, oxidizing agents and resistant to aerobic digestion. Hence, contaminations due to dyes pose not only a severe public health concern, but also many serious environmental problems because of their persistence in nature and non biodegradable characteristics **(Hajira et al., 2008**).

Organic compounds constitute a very large group of pollutants present in industrial and municipal wastewater. Many of them are recognized carcinogens and known to be toxic to the environment. Among the available methods for removing these pollutants, adsorption is still one of the most preferred methods, especially for effluents with moderate to low pollutant concentration **(Juang et al., 1996; Nouri et al., 2002**).

Fruit stones are appropriate raw materials for the production of activated carbons. The use of these materials as adsorbents of inorganic and organic pollutants from water is due to their unique versatility resulting from their high surface area, porous structure, high adsorption capacity, and surface chemical nature, which can be appropriately modified by physical and chemical treatments to enhance the extent of a given adsorption process **(Zoulikha M. and Fatima A., 2008**).

The use of adsorption contacting systems for industrial and municipal wastewater treatment has become more prevalent during the recent years **(Babu and Gupta, 2004**). An adsorption process is often used at the end of a treatment sequence for pollution control due to the high degree of purification that can be achieved. Adsorption is an important step in industrial downstream processing (**Gupta and Babu, 2006**). The adsorption process exploits the ability of certain solids called the adsorbents preferentially to concentrate specific substances called the adsorbates from solution onto their surfaces. The most widely used adsorbents are activated carbon, activated alumina, activated boxite, silica gel, polymers **(Nonhebal, 1972**), date pits **(Gaid, A., et al., 1994; Abdulkarim, M., et al., 2001**), porcellanite **(Mazin, K. M., 1998**), wool fiber and cotton fiber **(Rasheed Khan, et al., 2005**), treated sugarcane bagasse **(Saiful Azhar, et al., 2005; Consolin, et al., 2007**), and rubber seed shell **(Oladoja, N. A. and Asia, I. O., 2008**). The factors affecting adsorption are:

1. The physical and chemical characteristics of the adsorbent (i.e., surface area, pore size, chemical composition, etc.).
2. The physical and chemical characteristics of the adsorbate (i.e., molecular size, molecular polarity, chemical composition, etc.).
3. The concentration of the adsorbate in the liquid phase (solution).
4. The characteristics of liquid phase (pH, temperature).
5. The contact time of the system **(Bhatia, 2001**).

The transport and subsequent adsorption of adsorbate onto adsorbent particle consists of three main mechanisms **(Ivars, 1976; Scott and Paul, 1987**).

a. Transport through the fluid boundary layer to the external surface of the adsorbent particle.

b. Interparticle diffusion in the liquid phase (pore diffusion) and/or in the adsorbed state along the pore walls (surface diffusion).

c. Adsorption to the solid surface of the pore.

Adsorption processes are modeled using a variety of isotherm models, kinetic models and diffusion models. Many systems can be modeled using a number of classical isotherms such as Freundlich and Langmuir together with more complex isotherms. Similarly many adsorption processes can be modeled using simple kinetic processes as well as more complex diffusion processes.

1.2 Adsorption, Absorption, and Sorption

Absorption generally refers to two phenomena which are largely unrelated. In one case, it refers to when atoms, molecules, or ions enter some bulk phase - gas, liquid or solid material. For instance, a sponge absorbs water when it is dry. Adsorption is similar, but refers to a surface rather than a volume: adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or, more rarely, a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. Sorption encompasses both processes, adsorption and absorption. (**www. wiki.answers.com**).

1.3 Pollution with Methylene Blue Dye

Colored dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. There are more than (10,000) commercially available dyes with over 7×10^5 tones of dyes produced annually (**Robinson T. et al., 2001**). It is estimated that 2% of dyes produced annually are discharged in effluent from manufacturing operations whilst 10% is discharged from textile and associated industries (**Easton J. R., 1995**).

Neglecting the aesthetic problem, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water which interferes with the growth of bacteria to levels insufficient to biologically degrade impurities in the water. Colour in effluents can cause problems in several ways:

1. Dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration.
2. Dyes are inherently highly visible, meaning that concentration as low as 0.005 ppm capture the attention of both the public and the authorities.
3. Dyes absorb and reflect sunlight entering water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants **(Slokar Y. M., and Le Marechal M., 1998**). One of these dyes is Methylene blue (MB).

MB is slightly hazardous in case of skin contact (irritant), of eye contact (irritant), and of ingestion and inhalation. Mutagenic for mammalian somatic cells and bacteria and/or yeast. Repeated or prolonged exposure is not known to aggravate medical condition (**Material safety data sheet, 2006**).

MB causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, painful micturition, and methemoglobinemia (**Ghosh and Bhattacharyya, 2002**). Therefore, the treatment of effluent containing such dye is of interest due to its aesthetic and environmental impacts on waters (**Tan, et al., 2007**). Colored effluents receive special attention because they are easily detected and on the other hand, the chemical structure of such dyes varies enormously. Certain methods can work very well for the uptake of a specific group of dyes but sometimes they can be inefficient to remove other different types of dyes. Adsorption methods have received great attention because they are effective and their application processes are relatively simple (**Consolin et al., 2007**).

1.4 Importance of the Study

Adsorption onto activated carbon has been found to be superior for water and wastewater treatment compared to other physical and chemical techniques which possess inherent limitations such as high cost, formation of hazardous by-products and intensive energy requirements. These techniques include flocculation, coagulation, precipitation and ozonation. However, commercially available activated carbons are still considered expensive. This is due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications. Therefore, in recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheap precursors which are mainly industrial and agricultural by-products, such as date pits, silk cotton hull and maize, jute fiber, ground-nut shell, corncob, bamboo, rattan saw-dust, and oil palm fiber **(Tan I.A.W. et al., 2007**).

The advantage of using agricultural by-products such as date pits as raw materials for manufacturing activated carbon is that these raw materials are renewable and potentially less expensive to manufacture, in addition to the fact that Iraq is one of the leading countries engaged in growing palm-date trees. It is noteworthy that very limited attempts were carried out for using Iraqi date pits for wastewater treatment purposes. Dates, which are produced from palm trees, are considered as a major source of food. Huge quantities of date pits are generated as wastes once dates are eaten. The generated pits can be reused to produce activated carbon that can be used for treating polluted water. Thus, the waste, which is the pits, can be utilized for producing activated carbon and “could” replace the imported activated carbon. The importance of this lies in using a treated local waste, which is the pits, as a medium for treating purposes. Thus, it will have an advantage from environmental and economical aspects.

As far as the economical aspect of the production of activated carbon from the local palm-date pits is concerned, it is evident that the production cost of the local pits is much less than the commercial activated carbon. This is due to the fact that the date pits in Iraq are considered as useless waste generated during the consumption and processing phases. Furthermore, the cost of importing commercial activated carbon from outside Iraq is so high, which reflects on the overall cost of production of activated carbon.

On the other hand, Iraqi siliceous rocks (Porcellanite) are abundantly and naturally available in the western region of Iraq. Furthermore, no studies have reported the use of Iraqi porcellanite rocks for dye adsorption from wastewater. This shows the importance of this research in utilizing locally available and cheap material for water and wastewater treatment purposes.

1.5 Research Objectives

The main objectives of this work can be summarized by the following points:

1. Using cheap and locally available materials for the removal of methylene blue dye from wastewater.
2. Making use of huge quantities of agricultural by-products (palm date-pits) for the production of activated carbon.
3. Minimizing the importing of expensive commercial activated carbon.

For achieving these objectives, the following steps were carried out during the present research:

1. Production of activated carbon from Iraqi palm-date pits.
2. Using the produced activated carbon for the removal of methylene blue dye from wastewater by adsorption in fixed bed.
3. Using Porcellanite rocks for the removal of methylene blue dye from wastewater by adsorption in fixed bed.
4. Making a comparison between the removal efficiencies of methylene blue dye from water using commercial activated carbon, the locally produced activated carbon and porcellanite.

CHAPTER TWO

THEORETICAL CONCEPTS AND LITERATURE REVIEW

2.1 Water and Wastewater Pollution with Dyes

Growing concern about environmental issues has prompted the textile industry to investigate appropriate and environmentally friendly treatment technologies. Waste aqueous effluent containing colour compounds causes serious environmental problems. A large variety of dyestuffs can be found in real effluents such as acid, basic, reactive, direct, etc. It has been estimated that about (9%) of the total amount (450000 tons) of dyestuffs produced in the world are discharged in textile wastewater. The most frequently applied adsorbent for the removal of organic pollutants in wastewaters is currently activated carbon. However, activated carbon is an expensive material. The use of alternative and perhaps cheaper adsorbents is attractive (**Allen S. J., and Koumanova B., 2005**).

Coloured dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. There are more than (100,000) commercially available dyes with over 7×10^5 tones of dyes produces annually (**Robinson T. et al., 2001**). It is estimated that 2% of dyes produced annually are discharged in effluent from manufacturing operations whilst 10% was discharged from textile and associated industries (**Easton J. R., 1995**).

The rapid growth rate in the use of reactive dyes is due to the increasing use of cellulosic fibres and the technical and economic limitations of other dyes used for these fibres (**Bonneau M., 1995**).

The removal of organic colours by adsorption has recently become the subject of considerable interest (**Onal, 2006**). Dyes are chemicals which on binding with a material will give colour to the material. Dyes are ionic, aromatic organic compounds with structures including aryl rings which have delocalized electron systems. The colour of a dye is provided by the presence of a chromophore group. A chromophore is a radical configuration consisting of conjugated double bonds containing delocalized electrons. Other common chromophoric configurations include azo (-N=N-), carbonyl (=C=O); carbon (=C=C=); carbon-nitrogen (=C=NH or –CH=N-); nitroso (-NO or N-OH); nitro ($-NO_2$ or =NO-OH); and sulphur (C=S). The chromogen, which is the aromatic structure normally containing benzene, naphthalene, or anthracene rings, is part of a chromogen- chromophore structure along with an auxochrome. The presence of ionizing groups known as auxochromes results in a much stronger alteration of the maximum absorption of the compound and provides a bonding affinity. Some common auxochrome groups include –NH3, -COOH, -HSO3, -OH (**Al-Ghouti, 2004**).

2.2 Adsorption Process

In the adsorption process there is a mass transfer of solute from a solvent onto the surface of a solid adsorbent. The driving force may be the lyophobic (i.e. solvent-rejecting) character of the solute or the affinity of the solute for the solid, or a combination of both. Thus, the substances that are removed from waters and wastewaters by adsorption onto activated carbon are typically organic contaminants which may have a molecular structure comprised of both hydrophobic and hydrophilic parts. In such cases the hydrophobic part tends to be active at the surface and undergoes adsorption. Surfactants are the prime examples of this category of substance. And the second driving force element referred to above, namely the affinity of the solute for the solid, may be due to a surface charge effect, a mass attraction effect or a chemical reaction effect. The rate at which adsorption proceeds is considered to be diffusion-controlled. Thus, while adsorption equilibrium is quickly attained on exposed particle surfaces, the rate of equilibrium attainment on pore walls is slower, being governed by the rate of diffusion of adsorbate molecules through the capillary pore passages. Since virtually all the useful adsorptive surface area is within the pores the overall rate of adsorption is dependent on particle size- it varies reciprocally with the square of the particle diameter, increases with increasing concentration of solute, decreases with increase in temperature and decreases with decreasing molecular weight of solute. The rate of adsorption has also been found to be proportional to the square root of the time of contact. In addition it is affected by pH, decreasing with an increase in pH and being very poor at pH values above 9.0 (**Casey J.T., 1992 and kairk R.E. and Othmer D.F., 1947**).

Adsorption may be defined as the selective removal of a component of a fluid mixture by contacting the fluid with a solid adsorbent. Applications include the purification of drinking water, and removal of harmful pollutants from wastewater effluents. It also has application in air pollution control and many processes in chemical engineering (**McKay, 2001**). It is well known that liquid-phase adsorption is one of the most efficient methods or the removal of colours, odours and organic pollutants from process of waste effluents (**Juang and Tseng, 2001**). Adsorption plays an important role in industry, both in the removal of contaminants from a product and as a direct means of recovery of valuable substances. Its most important use is in the removal of organic contaminants from polluted sources. The removal of organic pollutants, particularly the synthetic variety, can be of particular significance to the environment. Most organic substances are ultimately biodegradable and can lead to oxygen depletion in receiving waters. Organic compounds can cause colour, taste and odour and large numbers of synthetic organic substances could have carcinogenic effects if the water is to be used downstream as a water supply or for packaged water (**Federal Register, 1987**).

The relative advantages of adsorption over other conventional advanced treatment methods are:

1. It can remove both organic as well as inorganic constituents even at very low concentrations.
2. It is relatively easy and safe to operate.
3. Both batch and continuous equipment can be used.
4. No sludge formation.
5. The adsorbent can be regenerated and used again (**Mohanty et al., 2005**).

Adsorption of a substance involves its accumulation at the interface between two phases, such as liquid and solid or a gas and a solid (**Bhatia, 2001**).

All adsorption processes involve a decrease in the free energy of the system. The decrease in the heat contain of the system is called the heat of adsorption (**Cassidy, 1951**).

2.3 Principle of Adsorption

The constituent that undergoes adsorption is referred to as the adsorbate and the solid into which the constituent is adsorbed is referred to as the adsorbent. During the adsorption process, dissolved species are transported into the porous solid adsorbent granule by diffusion and are then adsorbed onto the extensive inner surface of the adsorbent. Dissolved species are concentrated on the solid surface by chemical reaction (chemisorption) or physical attraction (physical adsorption) to the surface (**Richardson, 1989**).

If the bond that is formed between the adsorbate and adsorbent is very strong, the process is almost always irreversible and chemical adsorption or chemisorption is said to have occurred. On the other hand if the bonds that are formed are very weak as the bonds formed by Vander Waals forces, physical adsorption is said to have occurred. The molecules adsorbed by this means are easily removed or adsorbed, by a change in the solution concentration of the adsorbate and for this reason, the process is said to be reversible. Physical adsorption is the process that occurs most frequently in the removal of wastewater constituents by activated carbon (**Metcalf and Eddy., 1972**).

Exchange adsorption is one of the types of adsorption that is used to describe adsorption characterized by electrical attraction between the adsorbent and the adsorbate that means (ion exchange) (**Rao C. S., 1994 and Ludersen A. L., 1983**).

The heat of physical adsorption is usually in the range of (2-15) kcal/mol, and the heat of adsorption for chemisorption is usually in the range of (30-100) kcal/mol (**Graham D., 1959 and Wa'adalla, 2006**). Chemisorption is more specific because a chemical reaction occurs that entails the transfer of electrons adsorbent and adsorbate and a chemical bond with the surface can occur. The heat of adsorption for chemisorption is typically above 200 KJ/mole (**Treybel, 1981**).

2.4 Adsorbents used for Colour Removal

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. Adsorbents may be classified according to porosity. Non-porous adsorbents are materials such as glass and steel beads, and clay. Their relatively small external adsorptive surface areas limit their commercial applications. Porous adsorbents must have a high internal surface area which is accessible to the components being removed from the fluid (**Sirianuntapiboon et al., Article in press**). The high internal surface area of an adsorbent creates the high capacity needed for a successful separation or purification process. For practical applications, the range of internal surface area is normally restricted to about 300-1600 m²/g. such porous adsorbents may be carbonaceous or inorganic in nature, synthetic or naturally accruing (**Crittenden and Thomas, 1998**). And below, a review which evaluates a number of different adsorbents and types of dyes. The review also outlines some of the fundamental principles of dye adsorption onto adsorbents:

2.4.1 Activated Carbon

Activated carbon has been used as an all-purpose sorbent. It is "hydrophobic." Its precedent, charcoal, was first used in the sugar industry in England in 1794 to decolorize sugar syrup. The major development of activated carbon took place during World War I, for use in filters to remove chemical agents from air. The commercial activated carbon has taken its present form since the 1930's (**Ralph T. Yang, 2003**). By the late 1930's there was considerable industrial-scale use of carbon for gaseous and liquid phase application and new manufacturing processes had been developed to satisfy the needs of industry. During the 1939-1945 war, a further significant development took place - the production of more sophisticated chemically impregnated carbon for entrapment of both war and nerve gases (**www.cameroncarbon.com**).

Activated carbon can be regenerated either chemically or thermally. In chemical regeneration, the carbon is contacted with chemicals that dissolve or oxidize the adsorbed impurities, while thermal regeneration proceeds by three major steps: vaporization of water near 100°C, baking of the adsorbate at temperature up to 800°C, and activation between temperatures of 800 and 950°C. During the baking step, the organic adsorbates are converted to a volatile fraction and free carbon residues on the surface (**Eckenfelder, W. W., Jr., 1966**).

The porous structure and chemical nature of an activated carbon is a function of the raw materials used in its preparation and the activation method used. This is the reason why surface area or pore volume of activated carbons can vary widely from one kind to another. Pore structure of activated carbon is shown in Fig.(2-1). (**Yagsi, 2004**).

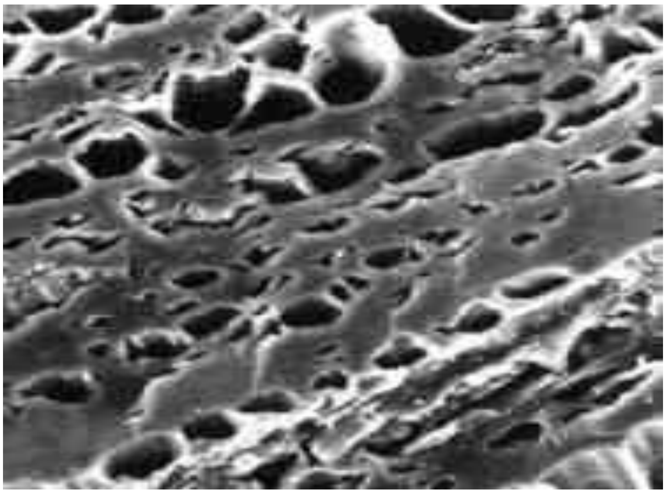


Fig. (2-1) Pore Structure of Activated Carbon (Yagsi, 2004)

The activated carbon particle has three types of pores existing in it by which adsorption take place. Conventional classification of pores according to their diameters, originally proposed by Dubinin and now officially adopted by the International Union of Pure and Applied Chemistry, (IUPAC) is mostly used and it is shown in Table (2.1) (**Reinoso, 1985**).

Table (2.1) Pore Sizes of Activated Carbon

Macropores	Pores with diameters >50 nm (500 Å)
Mesopores	Pores with diameters 2-5 nm (20-500 Å)
Micropores	Pores with diameters <2 nm (20 Å)

The macropores provide a passageway to the particle's interior and to the micropores but do not contribute substantially to the particle surface area. The micropores, on the other hand, are responsible for the large surface area of activated carbon particles and are created during the activation process. It is in the micro pores that adsorption largely takes place (**Carbon adsorption handbook, 1978**). Fig.(2-2) shows micro, meso and macropore regions of activated carbon.

Different physical forms of activated carbon are produced depending on their application: granular forms (GAC) to be used in adsorption columns and powder (PAC) forms for use in batch adsorption followed by filtration.

The adsorption of two basic dyes, Maxilon Schwarz FBL-01 (MS-300) and Maxilon Goldgelb GL EC (MG-400), from aqueous solution by granular activated carbon and a natural zeolite in batch processes demonstrate that the activated carbon has a much stronger affinity for the dyes than the zeolite by a factor of two (**Meshko V. et al., 2001**).

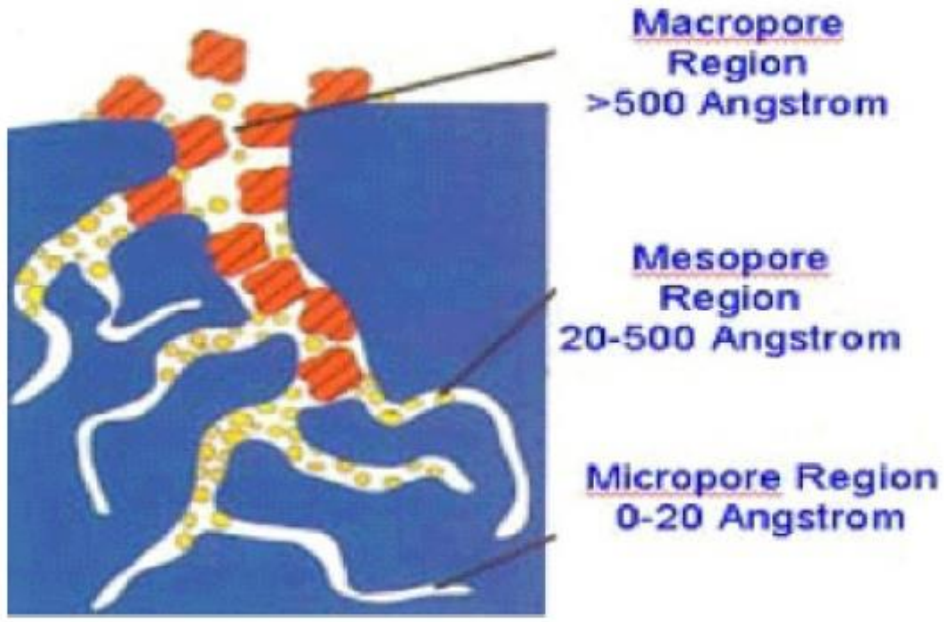


Fig.(2-2) Micropore, Mesopore and Macropore Regions of Activated Carbon (Reinoso, 1985)

(**Meshko et al., 2001**) continue that the saturation capacities for both adsorbents for MG-400 are lower than for MS-300, because of the higher concentration of the active coloured material in the commercial salt of the MG-400. The major component in MG-400 is a branched molecule which is also present in MS-300 but in significantly lower levels. It is therefore suggested that the molecules of MG-400 are probably unable to penetrate easily into the pores of the adsorbents where as the molecules of MS-300 will have less hindrance. Overall, the size of both dye molecules is such that the adsorption is hindered and capacity is reduced due to pore blockage. The higher adsorption capacity of the activated carbon is attributed to the better pore size distribution in comparison to that of the zeolite.

(**Walker G.M., and Weatherly L.R., 1999**) measured the kinetics of acid dye adsorption onto a granular activated carbon. They report that a single value of a solid diffusivity could be used to describe the adsorption decay curves for constant mass contacting systems. However a decrease in solid diffusivity was required or systems with different initial dye concentrations. Chemisorption was suggested as the likely mechanism for the acid dye removal from water.

In a separate paper, (**Walker G.M., and Weatherly L.R., 1997**) report that the adsorption of the acid dyes by granular activated carbon in a fixed bed contacting system was characterized by shallow breakthrough curves suggesting a large mass transfer zone and the possible inefficient use of the carbon. The adsorption of dyes onto carbon can depend upon surface charge of the carbon in the presence of water. This will be close to neutral and physical adsorption will predominate. Hence, active carbons will demonstrate a high capacity for both acid and basic dyes (**McKay G., 1982**).

(**Choy et al., 1999**) considered the adsorption of acid dyes onto granular activated carbon and presented an analysis of the equilibrium adsorption in single component and multi-component solutions. The data were analyzed for three dyes using the Langmuir, Freundlich, Redlich-Peterson, Tempkin and Dubinin-Radushkevich isotherms. In their work the Redlich-Peterson isotherm was demonstrated to provide the best correlation for the sorption process. For the multi-component isotherm models, an extended Langmuir model proved to be successful in predicting the binary equilibrium data.

(**Al-Degs et al., 2000**) investigated the effect of carbon surface chemistry on the adsorption of three reactive dyes in aqueous solution. In this work, the adsorption capacities for anionic reactive dyes, namely Remazol Golden Yellow RNL (Reactive Orange 107), Remazol Red RD (Reactive Red 198) and Remazol Black B (Reactive Black 5) were determined using Filtrasorb-400 activated carbon. Under the same conditions, the adsorption capacity decreases in following manner: Remazol Yellow> Remazol Black> Remazol Red.

The adsorption capacity for reactive dyes increased with a decrease in the carbon particle diameter. At a particle size range of 300-500 mm the values of saturation capacities are reported as 1111, 434, and 400 mg/g for reactive yellow, reactive black and reactive red respectively. F-400 has a high adsorption capacity for these dyes compared to chitosan where reported values are 380, 179 and 87 mg/g for reactive red, reactive yellow and reactive black at a particle size of 250-420 mm respectively (**Juang R.S. et al., 1997 and Rorrer G.L. et al., 1993**).

(**Al-Degs et al., 2000**) indicate that the adsorption capacity for Remazol dyes on granular activated carbon F-400 was reduced upon mixing in multi-component solutions. The results also show that carbon affinity was still higher for Remazol yellow followed by Remazol black and is lowest for Remazol red. This effect was also reported in a study of three dyes (anionic character) in binary and ternary mixtures. The adsorption capacity of the individual dye from any mixture was lower than sorption from a single component system for all dyes studied (**Shore J., 1996**).

(**Allen S.J. et al., 1988**) considered the competitive adsorption of three basic dyes. The results showed that the adsorption capacity of an individual dye decreased in the presence of a second or a third dye. The reduced capacities can be attributed to a number of factors including: interaction between the dyes in solution, change of the adsorbent surface charge due to adsorption, competitive adsorption between the dyes for active sites on the carbon surface where displacement effects replace the other dyes from the adsorption sites.

Activated carbon made from delayed petroleum coke is considered to be effective in the removal of colour from pulp bleaching water (**Shawwa A.R. et al., 2001**). Methylene blue adsorption capacity of the activated petroleum coke was ten times grater than that for the raw petroleum coke. Activated carbons produced from various agricultural wastes such as silk cotton hull and coconut tree sawdust, sago waste, maze cob and banana pith, have been used for the removal of dyes from aqueous solutions(**Kadirvelu K. et al., 2000**). However, despite the overriding influence of the nature of raw materials on the characteristics of the finished product, the search for low cost more environmentally friendly adsorbents has lead to the use of cocoa shell, coconut shell, fruit stones, newspapers, old tyres and basically any carbonaceous material remaining from industrial and/or municipal processes (**Pollard S.J.T. et al., 1992**). Choice of raw materials depends on what is available locally at low cost.

2.4.2 Chitin and Chitosan

Chitin is a naturally occurring derivative of cellulose, where the C_2 hydroxyl group has been replaced by the acetyl amino group $NHCOCH_3$. The major derivative of chitin is chitosan which refers to a family of polymers deriver from chitin by deacetylation. Chitin and chitosan are adsorbents which can contain amine or amide nitrogen in varying proportions. These groups can lead to the adsorbents having a larger adsorption capacity for acid dyes or anionic dyes. Adsorption can occur by van der waals attraction, hydrogen bonding and columbic attraction (**Giles C.H. et al., 1958 and Bousher A. et al., 1997**). Chitin will display no significant attraction to basic dyes (**McKay G. et al., 1982**). Chitin contains the amide group -CO-NH- which cannot be easily protonated. The electron withdrawal by the carbonyl group makes the nitrogen of the amide group a poorer source of electrons than that of the amine group. Fewer electrons are available for sharing with a hydrogen ion and therefore the amide is a much weaker base than the amine group. Hence in Chitin there is less electrostatic attraction between the Chitin and the dye anion.

2.4.3 Diatomite

Diatomite is siliceous sedimentary rock consisting principally of the fossilized skeletal remains of the diatom (**Closceri L.S. et al., 1989**). Total surface area of diatomite is around 28 m^2/g. More importantly however is the presence on the silica surface of silanol groups that spread over the matrix of the silica (**Al-Degs Y. et al., 2001**). The silanol group is a very active group, which can react with many polar organic compounds and various functional groups. This property makes it a possible adsorbent for many dyes.

The feasibility of using diatomite for the removal of Cibacron reactive black C-NN (RB) and reactive golden yellow MI-2RN dye as well as methylene blue, a basic dye is reported (**Al-Ghouti M. et al., 2003**). Unfortunately, the molecular structure of Cibacron reactive black and yellow dye is not released, however it is expected that most Cibacron reactive dyes contain a reactive halotriazinyl amine group that has two or more labile chlorine atoms activated by the electron withdrawing action of the three N atoms. Diatomite has surface charges which may arise from chemical reactions at the surface due to the presence of ionisable functional groups such as –OH, -COOH, -SH and $–NH_2$. The ionization of such groups results in electric charges (**Leon C. and Radovic L., 1994**).

The surface charge caused by these surface chemical reactions is known as the surface charge density which is dependent on the degree of ionization and on the pH of the system. For diatomite, the zero point of charge (pH_{zpc}), the pH at which the total charge from the cations and anions at the adsorbent surface is equal to zero, occurred at pH value of 6.2. The surface charge density decreased as the pH increased. Hydroxyl groups present on the surface of the diatomite can gain or lose a proton resulting in a surface charge that varies with changing pH. At low pH, surface sites are protonated and the surfaces become positively charged. At high pH, the surface hydroxides lose their protons and the surface becomes anionic. The effect of initial dye concentration on the ability of diatomite to adsorb dyes from solution suggests that the percentage colour removal of methylene blue decreased when the initial dye concentration increased. However, it remained constant in the dye concentration range 100-1000 mg/l for the reactive dyes. The adsorption isotherm data were further analyzed using the Langmuir and Freundlich isotherms, which are the most frequently applied sorption isotherm models. The adsorption behavior of methylene blue, hydrolyzed reactive black and yellow dyes were favorable. It seems that diatomite has a high selectivity for basic and reactive dyes. The Langmuir isotherm was unable to explain the adsorption process for the reactive dyes but was suitable for the basic dye. It is important to recognize that the mechanism of dye adsorption on diatomite cannot be concluded directly from the Langmuir or Freundlich fitting, however it can be concluded that the adsorption isotherm of methylene blue exhibits Langmuir behavior, which indicates a monolayer adsorption (**Benefield and Weand, 1982**). Adsorption of methylene blue onto diatomite can be attributed to the formation of surface hydrogen bonds of the hydroxyl group on the diatomite surface and the nitrogen atoms of methylene blue. The affinity of methylene blue, hydrolyzed reactive black and yellow dyes for diatomite were methylene blue > hydrolyzed reactive black > hydrolyzed reactive yellow (**Al-Gouti et al., 2003**).

2.4.4 Silica

Silica is used as an adsorbent mainly in granular form. Sorbsil silica gel is reported to adsorb basic dyes (**McKay et al., 1980**). The rate of adsorption of Astrazone blue, a basic dye, on sorbsil silica has been studied in batch adsorbers. Parameters studied include particle size, initial dye concentration, agitation and dye solution temperature. The rate-controlling step is mainly intraparticle diffusion, although a small boundary layer resistance is experienced. The process shows the same general form of an initial steep rise in adsorption with time and then a rapid leveling off as equilibrium is established. In all cases 90% of the equilibrium value is reached after 240 minutes of contact (**McKay et al., 1977**).

2.4.5 Perlite

Perlite is an amorphous siliceous mineral silicate and the feasibility of the electro-adsorption of acilan blue dye by perlite-activated carbon mixtures suggests that the process is better than activated carbon alone (**Koparal et al., 2002**).

2.4.6 Dolomite

(**Walker et al., 2003**) report on the kinetics of adsorption of a reactive red dye by dolomite and dolomitic adsorbents. Results indicated that dolomite and charred dolomites have the potential to act as adsorbents for the reactive dye. The removal rate appears to be dependent on both an external mass transfer process and some intraparticle diffusion. A comparison is made with uptake using a Chemviron activated carbon indicating that the adsorption by the dolomite char is greater than that of activated carbon and dolomite.

2.4.7 Fuller's earth

Fuller's earth is a natural clay which can contain variable amounts of dioctahedral smectites, natural zeolites and other sepiolites. The main content is magnesium and aluminum silicates. The clay is given an open porous structure by heating and drying processes. Methylene blue, a cationic dye, is shown to adsorb strongly onto four different Fullers earth samples of varying compositions (**Atun et al., 2003**). Methylene blue adsorption appears to increase as the percentage of Al_2O_3, CaO and Fe_2O_3 in the Fuller's earth decreases and as the percentage of MgO and Na_2O decreases. Both the Langmuir and Freundlich isotherms gave good agreement.

2.4.8 Bentonite

Bentonite is a fine powder clay which normally requires activation by acid washing before it exhibits adsorptive properties. The clay has adsorbent properties and an alkaline pH due to the presence of sodium, potassium and calcium components. Bentonite has been used for dye removal from water (**Ramakhrishna and Viraraghavan, 1997**). In this work, peat, steel plant slag, bentonite clay, fly ash and activated carbon adsorbents were compared in batch kinetic studies, isotherm studies and column studies and the data were evaluated for compliance with the Langmuir, Freundlich and BET isotherm models. Acid, basic and disperse dyes were used and the results showed high removals of acid dyes by fly ash and slag while peat and bentonite exhibited high basic dye removals. For the acid and basic dyes, the removals were comparable with that of granular activated carbon, while for the disperse dyes, the performance was much better than that of granular activated carbon.

2.4.9 Zeolite

Mezoporous materials such as sepiolite and zeolite which are highly porous materials have been used to adsorb three reactive dyes (**Ozdemir O. et al., 2004**). Adsorption isotherms for natural sepiolite exhibit a linear increase followed by a plateau region. The results reveal that natural sepiolite appears to have little affinity for reactive dyes. The natural zeolite appears to have a negative adsorption except for the red dye above 25 g/l.

2.4.10 Peat

Peat is a low grade carbonaceous fuel containing lignin, cellulose and humic acids as its major constituents. These constituents are potentially very useful from an adsorption standpoint as they bear polar functional groups such as alcohols, aldyhides, carboxylic acids, ketones, and phenolic hydroxides which can all be involved in chemical bonding with the adsorbed pollutants. Peat has a polar character which lends itself to the adsorption of specific materials such as metals and polar organic molecules.

Peat is known to have excellent ion exchange properties similar to natural zeolite (**Belkevich et al., 1976**). Adsorption of a cationic dye appears to increase with increase in pH consistent with a mechanism of adsorption by cation exchange with acidic functional groups. There are then more adsorption sites for cation uptake from solution. Peat is shown to be particularly effective adsorbent for basic dyes but has a lower capacity for acid dyes (**Huang et al., 1978**).

2.4.11 Lignite

Lignite is a member of the solid fuel family and is often referred to as brown coal. The surface area, porosity, functional groups, calcium and magnesium ion content all contribute to its adsorption properties. Lignite has a strong affinity for basic dyes (**Allen et al., 1989**). The Lignite-cationic dye adsorption process is facilitated by the presence of humic acid groups in the lignite. The adsorption process is a function of the dye structure and the lignite structure. Different ions will experience different physical and electrical attractive and repulsive forces according to their structure, molecular size and functional groups.

2.4.12 Other Adsorbents

Materials such as charred sawdust, carbonizes wool waste (**Nag and Trans, 1995**), charred plant material (**Malmary G. et al. 1985**), quaternized rice husk (**Perineau F. et al., 1982**) and cassava peel char (**Low and Lee, 1997**) have been found to be effective in the removal of a variety of dyes from water. Materials that have been used in their natural state to adsorb heavy metals and dyes from solution include linseed cake (**Liversidge et al., 1997**), sunflower stalks (**Sun G. and Xu, 1997**), banana peel (**Namasivayam et al.1993**), orange peel (**Annadurai G. et al., 2002**) and maize cob (**Nassar and Al-Geundi, 1991**).

2.5 Production of Activated Carbon

Various methods are available for the activation process but the most widely used are the treatment of the carbonaceous material with oxidizing gases such as air, steam or carbon dioxide and the carbonization of the raw materials in the presence of chemical agents such as Zinc chloride, Magnesium chloride, Calcium chloride or Phosphoric acid. The raw material is mixed with the chemical agent, dried and calcined at temperatures up to 900°C. Other methods such as activation of the carbonaceous materials or chars mixed with Potassium hydroxide hydrate as activating chemical treatment of char with sulphur vapour at elevated temperatures and subsequent desulphurization with hydrogen and activation in an inert atmosphere under reduced pressure without the use of any chemical activator are reported. Treatment of charcoal and carbon black with oxidizing solutions such as nitric acid or a mixture of nitric and sulphuric acid also increase the surface area as well as introduce acidic oxides (carboxylic, phenolic and quinonic) to the carbon surface (**Lartey and Francis, 1999**).

2.5.1 Raw Materials

The quality of the resulting activated carbon is considerably influenced by the raw material. Although the activation procedure employed mainly determines the chemical nature of the surface oxides and the surface area of the resultant product, the structure of the pores and the pore size distributions are largely predetermined by the nature of the starting material. Any cheap substance with a high carbon and low ash content can be used as a raw material. Raw materials for the production of activated carbon include number of carbonaceous materials, especially wood, peat, brown coal, bituminous coal, lignite, coconut shells, almond shells, pits from peaches and other fruit, petroleum-based residues and pulp mill residues.

Table (2.2) Fixed Carbon Contents of Raw Materials Employed in Activated Carbon Manufacture (Holden, 1982)

Material	***Percent carbon content***
Soft wood	40
Hard wood	40
Coconut shell	40
Lignite	60
Bituminous coal	75
Anthracite	90

Fixed carbon contents of some raw materials are given in Table (2.2). On the other hand, the younger fossil materials-wood, (mainly birch wood and beech wood) peat and wastes of vegetable origin (such as fruit stones, almond shell, coconut shell, saw dust) can be activated easily and give high quality products (**Holden, 1982, sited in Yagsi, 2004**).

2.5.2 <u>Production Methods</u>

Activated carbon can be prepared by one of the following two methods:

- Carbonization after addition of substances. In this method, the activation agent like $ZnCl_2$, H_3PO_4, KOH, K_2S or KCNS that has to be applied in large quantities has to be removed via washing in order to reveal the porous structure and to make the material practically applicable. This route is generally called “chemical activation.”

- Partial gasification, generally called “physical activation.” The activation agents most often used are steam, carbon dioxide, and air or a combination of these (**Çuhadar, 2005**).

2.5.3 Chemical Activation

In chemical activation the precursor is impregnated with a given chemical agent and pyrolyzed after that. Several activating agents have been reported for the chemical activation process: phosphoric acid, zinc chloride and alkaline metal compounds. Phosphoric acid and zinc chloride are activating agents usually used for the activation of lignocellulosic materials which have not been previously carbonized; while, alkaline metal compounds, usually KOH, are used for activation of coal precursors or chars. An important advantage of chemical activation is that the process normally takes place at a lower temperature and for a shorter time than those used in physical activation. In addition, very high surface area activated carbons can be obtained. Moreover, the yields of carbon in chemical activation are 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.

On calcinations, the impregnated chemicals dehydrate the raw materials, which results in changing and aromatization of the carbon skeleton by the creation of a porous structure and surface area. However, the general mechanism for the chemical activation is not so well understood as for the physical activation. Other disadvantages of chemical activation process are the need of an important washing step because of the incorporation of impurities coming from the activating agent, which may affect the chemical properties of the activated carbon, and the corrosiveness of the chemical activation process.

An important factor in chemical activation is the degree of impregnation. This weight ratio of the anhydrous activation agent to the dry materials is defined as the coefficient of impregnation. The effect of the degree of impregnation on the porosity of the resulting product is apparent from the fact that the volume of salt in the carbonized material is equal to the volume of pores, which are freed by its extraction. For small degrees of impregnation, a small increase in impregnation amount causes an increase in the total pore volume of the product showing an increase in the volume of smaller pores. When the degree of impregnation is further raised, the number of larger diameter pores increases and the volume of the smallest pores decreases. The activated carbons produced through chemical activation, especially when $ZnCl_2$ is used, must be cleaned from the chemical agent before their commercial use. One advantage of using phosphoric acid in chemical activation is that, it can be cleaned from the activated carbon by rinsing with boiling pure water (**Çuhadar, 2005**).

2.5.4 Physical Activation by Carbonization

The method of production of the carbonized intermediate product has a marked effect on the quality of the final activated carbon product. The main aim of carbonization is to reduce the volatile content of the source material in order to convert it to a suitable form for activation. During the phase of the carbonization, carbon content of the product attains a value of about 80 percent.

By carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material and the freed atoms of elementary carbon are grouped into organized crystallographic formation known as elementary graphitic crystallites. Carbonization of lignocellulosic material starts above 170°C and it is nearly completed around 500°C- 600°C (**Smisek and Cerny, 1970; Wigmans, 1985**).

2.5.5 Previous Works on Preparation of Activated Carbon

(**Al-Attas, O., 2003**) prepared activated carbon from Saudi palm date pits. The pits were initially boiled in a pressure cooker for 2 hours and then soaked in a (85% phosphoric acid) for 12 hours and 24 hours respectively. After the soaking period, the pits were placed on a metallic plate and subjected to an average temperature of 400°C for 3 hours. The carbonized pits were then cooled and washed with hot water until the desired pH was achieved (5.5-8.5). He studied the feasibility of using the produced activated carbon for the removal of methylene blue dye from water. This test has been conducted to check the ability of the produced activated carbon (24-hr and 12-hr acid soaked pits) to remove the pollutants. The experiment lasted for 12 days for both the 24-hr and 12-hr acid soaked pits compared to the commercial activated carbon, which lasted for 35 days.

To investigate the pollutant removal efficiencies of the produced activated carbon, an experiment was performed by allowing an unchlorinated secondary effluent to pass through three columns, each filled with different types of activated carbon (i.e. 24-hr acid soaked pits, 12-hr acid soaked pits and commercial activated carbon). The experimental run continued for a period of seventeen days. All three columns were run simultaneously. The run was terminated when the breakthrough was reached. The samples taken from all ports were analyzed for pH and TOC on a daily basis, whereas the Total Coliforms and the BOD were monitored on alternate days only. The BOD and TOC average removals in the 24-hr acid soaked pits, 12-hr acid soaked pits and the commercial activated carbon were 71%, 69% and 73%, respectively. With regard to total coliforms, very good removal rates were achieved in all columns packed with the three types of carbon in the first few days. However, the removal rates decreased signaling the breakthrough conditions.

(**Girgis et al., 1998**) carbonized phosphoric acid impregnated apricot stones at 300, 400 and 500°C. For impregnation, a ratio of acid volume: weight of raw precursor of 1.5/1 was employed and it was observed that, as the temperature increased the BET surface area increased from 700 m^2/g up to 1400 m^2/g. In this study, they used 20%, 30%, 40% and 50% phosphoric acid by weight. The highest BET surface area was obtained from the sample which was impregnated with 30% phosphoric acid and carbonized at 500°C.

(**Girgis et al., 2002,** sited in **Çuhadar, 2005**) obtained activated carbon from date pits by using phosphoric acid. The raw material was impregnated with increasing concentrations of H_3PO_4 (30-70 wt. %) followed by pyrolysis at 300, 500 or 700°C. Carbons obtained at 300°C were very poorly porous, although with high capacity for the uptake of probe molecules from solution. Carbons obtained at 500 and 700°C were found to be good to excellent adsorbents. The best porosity development was found at 700°C with 50 wt. % H_3PO_4 impregnated sample having 945 m^2/g of BET surface area.

(**Bevla et al., 1984 a,b** sited in **Yagsi, 2004**) produced activated carbon from almond shells through chemical activation. Among several activating agents (H_3PO_4, $ZnCl_2$, K_2CO_3 and Na_2CO_3), $ZnCl_2$ activation gave the best products with high adsorption capacities. Raw material particle size, activation time and impregnation ratio were studied, showing the impregnation ratio to be the most effective variable in increasing the adsorptive power of the products up to 2111 m^2/g. It was observed that, activating reagent recovery and adsorptive capacity increased as the raw material particle size decreased. A maximum adsorption capacity had been observed at 500°C.

(**Johns et al., 1998**) produced granular activated carbons (GACs) from low value agricultural by-products and used them for environmental remediation. They characterized and evaluated the GACs as effective removers of organics and metals from water. The by-products included rice straw, soybean hull, sugarcane bagasse, peanut shell, and harder materials such as pecan and walnut shells. These byproducts were CO_2 or steam activated and then oxidized to enhance the metal adsorption. Table (2.3) summarizes the results of carbonization and activation additional to the surface area for the carbons activated. The results of this study indicated that the GACs made from selected agricultural by-products can be more effective than commercial GACs in the adsorption of organic and metal contaminants from water.

(**Warhurst et al., 1996**) worked on the production of activated carbon for water treatment in Malawi using the waste seeds of Moringa Oleifera (multi-purpose tree). They showed that the seeds of this tree could be used as a coagulant in water treatment. The same seeds can be converted into activated carbon by carbonization at 485 °C under N_2 for 30 minutes, followed by activation in steam at 850 °C for 5 minutes.

(**Teng and Yeh, 1998**) prepared activated carbons by chemical activation from two Australian bituminous coals. The preparation process consisted of zinc chloride impregnation followed by carbonization in nitrogen. The carbonization temperature ranged from 400 to 700°C. The experimental results revealed that an acid-washing process following the carbonization with $ZnCl_2$ is necessary for preparing high porosity carbons. Table (2.4) summarizes the effects of carbonization temperature on the surface properties of the carbons from $ZnCl_2$ activation. It was found that the surface area, pore volume, and average pore diameter of the resulting carbons increased with the carbonization temperature to a maximum at 500°C and then began to decrease with the temperature.

Table (2-3) Produced Granular Activated Carbons from Agricultural By-products (Johns et al., 1998)

Type of by-product	Char yield (%)	Activation temp. °C	Duration (hours)	Activant	Burn-off (%)	Surface area (m^2/g)
Peanut Shell Pellets	30	850	10	CO_2	17.3	127
Peanut Shell Pellets	30	800	12	steam	25.0	478
Rice Straw Pellets	35	850	10	CO_2	27.2	127
Rice Straw Pellets	35	800	12	steam	11.7	400
Sugarcane Bagasse Pellets	35	850	10	CO_2	20.3	490
Sugarcane Bagasse Pellets	35	800	12	steam	15.1	365
Soybean Hull Pellets	25	850	5	CO_2	27.2	38
Soybean Hull Pellets	25	800	12	steam	57.0	380
Walnut Shell	26	850	15	CO_2	20.7	456
Walnut Shell	26	800	12	steam	16.7	602
Pecan Shell	27	800	15	CO_2	34.0	547
Pecan Shell	26	800	12	steam	32.0	721

Table (2-4) Effects of Carbonization Temperature on the Surface Properties of two Australian Bituminous Coals by $ZnCl_2$ Activation (Teng and Yeh, 1998)

Carbonization Temperature (°C)	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore Diameter (Å)
(Type I)			
400	501	0.28	22
500	1300	0.83	25
600	895	0.55	24
700	858	0.49	23
(Type II)			
400	775	0.41	21
500	1080	0.65	24
600	994	0.58	23
700	874	0.50	23

(**Teng and Hsu, 1999**) also, prepared activated carbons by potassium hydroxide (KOH) activation from the same Australian bituminous coals. The preparation process consisted of KOH impregnation followed by carbonization in nitrogen. The carbonization temperature ranged from 500 to 1000°C for 0-3 hours. The surface area and pore volume of the resulting carbons were found to increase with the carbonization temperature to a maximum at 800°C and then begin to decrease. The optimum values of the surface area and the pore volume were found to be 3000 m2/g and 1.5 cm^3/g, respectively.

(**Johns et al., 1999**) applied the following activation techniques: (1) steam, (2) carbon dioxide (CO_2), and (3) phosphoric acid (H_3PO_4) to produce granular activated carbons (GACs) from pecan shell chars. All the three activation methods resulted in surface areas that were equal to or greater than commercial activated carbons as can be seen from Table (2-5). Carbon dioxide activation favored microporosity, while the other activations increased both mesoporosity and microporosity. All the three types were tested for the adsorption of metals (copper) and organic compounds. It was found that the GACs made from pecan shells by different activation methods can be more effective than commercial GACs in the adsorption of metal and organic contaminants from water.

Table (2-5): **Surface Areas of Commercial Carbons and Pecan Shell Carbons Activated by Steam, Carbon Dioxide and Phosphoric Acid (Johns et al., 1999)**

Pecan shell carbons	
Activation type	***Surface area (m²/g)***
Steam	1149
Carbon dioxide (CO_2)	877
Phosphoric acid (H_3PO_4)	1561
Commercial activated carbons	
Filtrasorb-400	944
GRC-20	928
RO 3515	791
Hydrodarco GCW	874
Hydrodarco 4000	575

(**Dai and Antal, 1999**) produced an activated carbon from macadamia nutshell charcoal by heating it in an inert environment to temperatures above 1000 K (> 900°C) for 25 minutes (“carbonized”), reacted with oxygen at temperatures between 525 and 586 K (252°C 313°C) for a period varying from 4.5 to 260 minutes (“oxygenated”), and heated again in an inert environment to temperatures above 1000 K (> 900°C) for 15 minutes (“activated”). According to this procedure, activated carbons with surface areas ranging between 101 and 138 m^2/g could be produced. The processing conditions employed (low oxidation temperatures, short processing times, and applying cheap activation agents) were found to be quite attractive compared to the conventional activation methods.

(**Mameri et al., 2000**) developed a process for producing high quality activated carbon from Algerian mill waste. The solid olive mill residue was carbonized at 800 °C and physically activated with CO_2, air or steam. An optimum activation temperature of about 850°C was determined for all the activation agents used. Steam appeared to be the most efficient activator as compared to air and CO_2. An optimal activation time of about 2 hours was then determined with steam as the optimum activation agent and the specific surfaces produced were exceeding 1500 m^2/g. Then, experiments were conducted on the adsorption of phenol into the activated carbon prepared. It was found that the activated carbon produced was effectively adsorbing the phenol solution that was prepared and the adsorption capacity was about 11.24 mg of phenol per gram of the activated carbon produced.

An activated carbon prepared from oil-palm shells was produced by (**Guo and Lua, 2000**). This type of carbon was produced by impregnating the oil-palm shells with potassium hydroxide (KOH). The preparation of the carbon started by crushing and sieving the oil-palm shells to different sizes. After impregnating with 10% KOH at room temperature for 24-hr, the shells were filtered, washed with hot water and dried. Thereafter, the sample was carbonized in a vertical tube furnace under a nitrogen flow. The furnace temperature was increased from room temperature to 600°C at the rate of 10°C/min maintaining this temperature for 2 hours. The resulting chars were activated with carbon dioxide at 800 °C for 1 hour to produce the final products. The surface area of the activated carbon produced was found to be 1408 m^2/g. The produced carbon was then used to study the adsorption of sulfur dioxide (SO_2). The experimental results showed that SO_2 could be adsorbed effectively by KOH-impregnated oil-palm shell activated carbons, whose adsorptive capacities were comparable to those of some commercial activated carbon.

Dates pits were used by (**Al-Omair and El-Sharkawy, 2005**) to prepare activated carbon using physical and chemical methods. The raw materials were physically activated with steam while the chemically activated samples were prepared in the presence of zinc chloride and phosphoric acid, individually. The textural properties, including surface area, mean pore radius and total pore volume, were determined. The adsorption of heavy metals including Cu^{2+}, Mn^{2+}, Pb^{2+}, Fe^{3+} and Cd^{2+} was studied in batch experiments. The type and amount of used activator had considerable effects on the textural characteristics of investigated samples, i.e. it develops the porosity and therefore changes the textural properties. These changes of textural properties were associated with an excellent removal efficiency, exceeds 90% and depending on the type of activator.

(**Al-Zahrani et al., 2000**) produced activated carbon from palm date pits. Chemical activation (by impregnation) using 70% phosphoric acid was followed by thermal treatment between 300 to 700°C. The effects of activation temperature and acid concentration on pore surface area development were studied. Samples prepared at 500°C showed a specific surface area of 1319 m^2/g and total pore volume of 0.785 cm^3/g. Aqueous phenol adsorption trends using the produced activated carbon sample were compared to a commercial sample (Filtrasorb-400). For phenol, the former exhibited a slightly higher adsorption capacity than the latter.

The feasibility of activated carbon prepared from oil palm shell to remove methylene blue from aqueous solutions was investigated by (**Tan et al., 2007**) through batch and column studies. The precursor was first washed to remove dirt from its surface and then dried overnight at 105°C. The dried shell was crushed and sieved to desired mesh size of 1–2 mm, then carbonized in a stainless steel vertical tubular reactor placed in a tube furnace under purified nitrogen (99.995%) flow of 150 cm^3/min at 700°C, with a heating rate of 10°C/min. The sample was held at the carbonization temperature for 2 h. The char produced was soaked in a potassium hydroxide (KOH) solution with an impregnation ratio of 1:1. The mixture was then dehydrated in an oven overnight at 105°C to remove moisture and then activated under the same conditions as carbonization, but to a final temperature of 850°C. Once the final temperature was reached, the nitrogen gas flow was switched to carbon dioxide and activation was held for 2 h. The activated product was then cooled to room temperature under nitrogen flow and washed with hot deionized water and 0.1 molar hydrochloric acid until the pH of the washing solution reached 6–7. Batch experiments were carried out to study the adsorption isotherm and kinetics at 30°C, with the initial concentration of 50–500 mg/l and solution pH of 6.5. Equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The equilibrium data were best represented by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 243.90 mg/g at 30°C. The adsorption process was found to be exothermic in nature. The kinetic data were fitted to pseudo-first-order, pseudo-second-order and intraparticle diffusion models, and it was found to follow closely the pseudo-second-order model. In column experiments, the effects of the initial dye concentration, bed height and flow rate on methylene blue adsorption were studied. The highest bed capacity of 40.86 mg/g was obtained using 100 mg/l initial dye concentration, 6 cm bed height and 20 ml/min flow rate.

(**Diya'uddeen et al., 2008**) produced activated carbon from corncobs by chemical activation. The precursors were carbonized in a carbonization rig (Carbolite HTR 11/75) for two (2) hours at 20°C/minute to a final temperature of 300°C and the weight loss of sample with temperature profile recorded. The carbonized samples were then physically impregnated with KOH pellets at ratio 1:3 precursors to activating agent and using distilled water, the mixture was made into a homogeneous moist sticky paste which was immediately charged into a furnace and heated slowly from room temperature to 110°C for (24) hours. The dried carbonized samples were then washed with distilled water and activated in the carbonization rig under nitrogen flowing at 20°C/min to a final temperature of 600°C, 700°C, 800°C and 900°C separately for (2) hours. Activated carbon produced was washed with distilled water and dried in an oven at 110°C overnight.

(**Yahia, 2006**) produced activated carbon from dates' stone by $ZnCl_2$ activation. The produced activated carbon was tested in batch study for the removal of methylene blue and phenol as adsorbates.

Bamboo, an abundant and natural resource in Malaysia, was used by (**Hameed et al., 2006**) for preparation of activated carbon. Bamboo was procured locally, washed, dried, and crushed to desired mesh size (1–2 mm). The raw material was then carbonized at 700 ◦C under nitrogen atmosphere for 1 h (first pyrolysis). A certain amount of produced char then was soaked with potassium hydroxide (KOH) at impregnation ratio of 1:1 (KOH pallets: char). The mixture was dehydrated in an oven overnight at 105°C; then pyrolysed in a stainless steel vertical tubular reactor placed in a tube furnace under high purity nitrogen (99.995%) flow of 150 cm^3/g (second pyrolysis) to a final temperature of 850°C and activated for 2 h. Once the final temperature was reached, the gas flow was switched to carbon dioxide and activation was continued for 2 h. The activated product was then cooled to room temperature under nitrogen flow and washed with deionized water to remove remaining chemical. Subsequently the sample was transferred to a beaker containing a 250 ml solution of hydrochloric acid (about 0.1 mol l^{-1}), stirred for 1 h, and then washed with hot deionized water until the pH of the washing solution reached 6–7.

Table (2-6) summarizes the raw materials, applications and the preparation methods used by different researchers to produce activated carbon, in addition to the surface areas of each type.

2.6 Previous Works on Porcellanite

(**Mohammed R. et al., 1999**) studied the removal of heavy metals discharged from many industries in Baghdad by adsorption onto a precoat filter of Iraqi siliceous rocks (Porcellanite) powder. This study showed the high ability of the Iraqi siliceous rocks to adsorb some heavy metals with about (99%) removal efficiency.

(Mazin K., 1998) studied the adsorption behavior of phenolic compounds by the Iraqi siliceous rocks powder. Adsorption isotherms of phenolic compounds were found to be fitted well with Langmuir model. This study showed that the Iraqi siliceous rocks powder can achieve high removal efficiencies with respect to phenolic compounds removal.

2.7 Adsorption Isotherm

The affinity of the adsorbate for an adsorbent is quantified using adsorption isotherms, which are used to describe the amount of adsorbate that can be adsorbed onto an adsorbent at equilibrium and at a constant temperature. For most applications in water treatment, the amount of adsorbate adsorbed is usually a function of the aqueous-phase concentration and this relationship is commonly called an isotherm. Several researchers have presented procedures, protocols and problem associated with performing adsorption equilibrium isotherms (**Crittenden et al., 1987a, Summers, 1986 and Luft, 1984**).

A liquid phase isotherm shows the distribution of adsorbate between the adsorbed phase and the solution phase at equilibrium. It is a plot of the amount of adsorbate adsorbed per unit weight of carbon (q_e)

versus the concentration of adsorbate remaining in solution (C_e) (**Chermisinoff and Ellerbusch, 1978**). Commonly, the amount of adsorbed material per unit weight of adsorbent increases with increasing concentration, but not in direct proportion, as shown in fig (2.3).

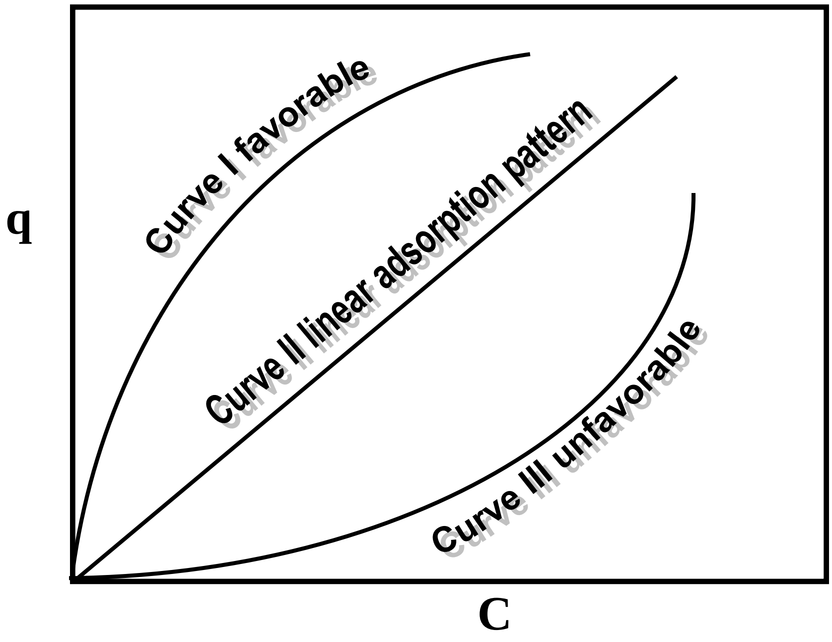


Fig. (2.3): Types of Sorption Separations (Weber, 1972)

Table (2-6): Summary of the Applications, Preparations and Surface Areas of Different Raw Materials Used in the Production of Activated Carbon

Raw material	*Application*	*Preparation*	*Surface area (m^2/g)*	*Reference*
Macadamia Nut and Coconut Shell	**Remove pollutants from gaseous and liquid streams**	**Physical activation using steam or CO2**	**> 1000**	**Tam and Antal, 1999**
Bituminous Coal		**Chemical activation using potassium hydroxide (KOH)**	**> 3000**	**Teng and Hsu, 1999**
Oil-Palm Shells	**Adsorption of sulfur dioxide (SO2).**	**Chemical activation using Potassium hydroxide (KOH)**	**520.6**	**Guo and Lua, 2000**
Macadamia Nutshell Charcoal		**Physical activation using air gasification**	**138**	**Dai and Antal, 1999**
Agricultural By-products	**Adsorption of dissolved metals and organics.**	**Physical activation using steam and CO2**	**38-970**	**Johns et al., 1998**
Bituminous Coals		**Chemical activation using zinc chloride (ZnCl2)**	**1300**	**Teng and Yeh, 1998**
Agricultural Wastes	**Gold mining and soft drinks industries.**	**Physical activation using steam, air or CO_2**	**1400**	**Lartey et al., 1999**
Oil-Palm Wastes	**Gas adsorption for air pollution control.**	**Physical activation using steam or carbon dioxide**	**970**	**Lua and Guo, 1999**
Olive Mill Solid Residue	**Phenol adsorption.**	**Physical activation using CO_2, air or steam**	**> 1500**	**Mameri et al., 2000**

Isotherm that is convex upward is called favorable, because a relatively high solid loading can be obtained at low concentration in the fluid. An isotherm that is concave upward is called unfavorable because relatively low solid loading are obtained and because it leads to quite long mass transfer zone in the bed. The linear isotherm goes through the origin, and the amount adsorbed is proportional to the concentration in the fluid. From these curves it will be noted that adsorption is a specific property depending upon the nature of adsorbate-adsorbent system (**Warren and Harriot, 1993**).

2.8 Adsorption Isotherm Models

The mathematical formulation of adsorption relationships are usually expressed in terms of either Freundlich or Langmuir equations.

The Freundlich equation has the general form: (**Casey T., 1992 and Ludersen A., 1983**).

$$\mathbf{q_e = x/m = kC_e^{1/n}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2\text{-}1)$$

Where:

q_e : The amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

x : The mass of the adsorbate. (mg)

m: The mass of the adsorbent. (mg)

C_e: equilibrium concentration of the solute remaining in solution. (mg/l)

K and n: are Freundlich constants with giving an indication of how favorable the adsorption process is. K (mg/g (l/mg)$^{1/n}$, is the adsorption capacity of the adsorbent which can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto the adsorbent for a unit equilibrium concentration. The slope of 1/n ranging between 0 and 1 is a measure of the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

The Freundlich isotherm, on the other hand, assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage (**Tan, et al., 2007**).

The equation which is more useful in logarithmic form is: (**Martine and Al-Bahrani, 1979**):

$$\log(q_e) = \log(x/m) = \log(k) + {}^{1}\!/_{n} \log C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2-2)}$$

A plot of (x/m) vs. concentration on Log-Log paper results in straight line with a slope of (1/n) and an intercept (k). The intercept is roughly an indicator of sorption capacity and the slope of adsorption intensity. Experimental data are often plotted in this manner as a convenient way of determining whether removal of material from solution is accomplished by adsorption and as means of evaluating the constant (k) and (n).

The Langmuir equilibrium adsorption equation has the form: **(Weber W. J., 1972**).

$$q_e = x/m = (Q_o\, b\, C_e)/(1 + b\, C_e) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2-3)}$$

The linearization form of the equation is (**Abdul-Hammed, H. M., 1996**):

$$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{1}{Qo} Ce \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2-4)}$$

Where:

C_e: The equilibrium concentration of the adsorbate (mg/l).

q_e: The amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

Q_o and b: are Langmuir constants related to the adsorption capacity and the rate of adsorption, respectively.

The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (**Tan, et al., 2007**).

A plot of (C_e/q_e) against (C_e) will give a straight line, the slope of which gives the value ($1/Q_o$) and its intercept with the (C_e/q_e) axis is the value of ($1/Q_o b$).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) (**Hameed et al., 2006**), which is defined by:

$$\mathbf{R_L = 1/(1+b\,C_o)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2-5)}$$

Where:
b is the Langmuir constant, and
Co is the highest dye concentration (kg/m^3).

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 ($R_L = 0$).

2.9 Adsorption in Fixed Bed

For fixed bed adsorption operation with activated carbon the water or wastewater to be treated is passed through a stationary bed of the carbon. An unsteady-state condition prevails in that the carbon continues to remove increasing amounts of impurities from solution over the entire period of useful operation (**Weber, W. J., 1972**).

These adsorbers give the advantages of simple operation plus the ability to serve as a filter for simultaneous suspended-solid removal

(**Kirk R. and Othmer D., 1947**). The column can be operated either under pressure or by gravity (**Martin, R. and NG W., 1985**). Fig (2-4) is a plot of the adsorption pattern normally obtained for a fixed-bed unsteady state adsorber (**Weber, W. J., 1972**).

The solute or impurity is adsorbed most rapidly and effectively by the upper few layers of fresh carbon during the initial stages of operation. These upper layers are of course in contact with the solution at its highest concentration level, (C_o). The small amounts of solute which escape adsorption in the first few layers of adsorbent are then removed from solution in the lower strata of the bed, and essentially no solute escapes from the adsorber initially.

The primary adsorption zone is concentrated near the top or influent of the column. As the polluted feed water continues to flow into the column, the top layers of carbon become practically saturated with solute and less effective for further adsorption. Thus the primary adsorption zone moves downward through the column to regions of fresher adsorbent. The wave, like movement of this zone, accompanied by a movement of the (C_o) concentration front, occurs at a rate, which is generally much slower than the linear velocity of the water or wastewater.

The plot of (C/C_o) versus time (for a constant flow rate) or volume of water treated depicts the increase in the ratio of effluent to influent concentrations as the zone moves through the column.

The break point on this curve represents that point in operation where-for all practical purposes-the column is in equilibrium with the influent water, and beyond which little additional removal of solute will occur. At this point it is generally advisable to reactivate or replace the carbon. Factors which affect the actual shape of the curve include the solute concentration, pH, and rate-limiting mechanism for adsorption, nature of the equilibrium conditions, particle size, the depth of the column of carbon and the velocity of flow.

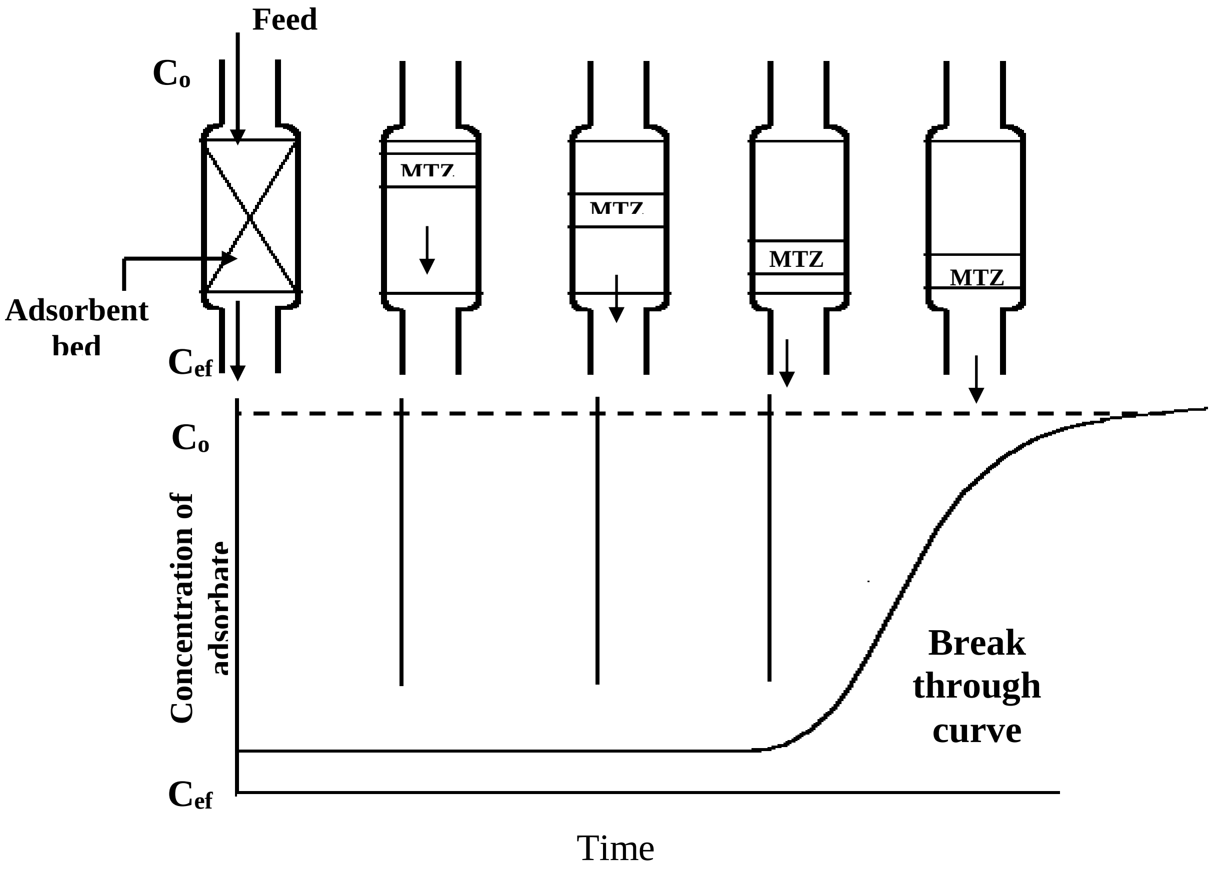


Fig (2-4): Schematic Representation of the Movement of the Adsorption Zone and the Resulting Breakthrough Curve (Afrah, 2005)

As a general rule, the time to break through point is decreased by: (**Treybal, R. E., 1981**).

- Increased particle size of the carbon.
- Increased concentration of solute in the influent.
- Increased pH of the water.
- Increased flow rate.
- Decreased bed depth.

If the total bed depth is smaller than the length of the primary adsorption zone required for effective removal of solute from solution, then the concentration of solute in the effluent will rise sharply from the time the effluent is first discharged from the adsorber.

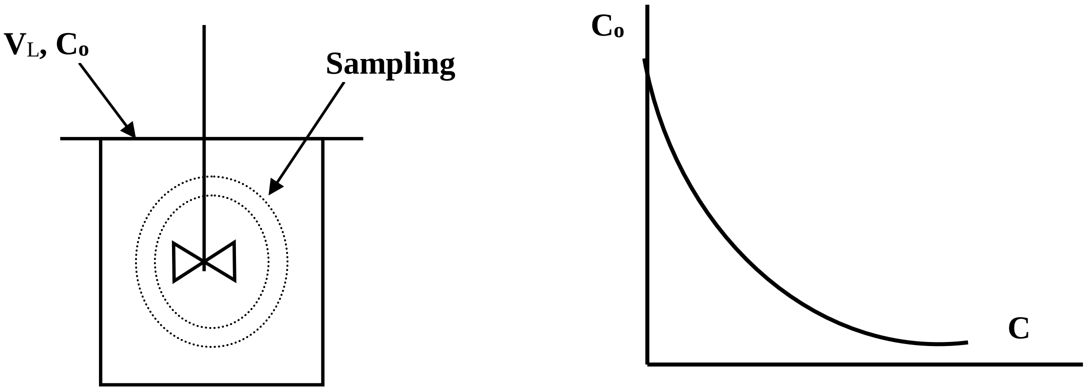
The break through point is often taken as a relative concentration of (0.05 or 0.1) and since only the last portion of fluid processed has this high a concentration, the average fraction of solute removed from the start to the break point is often (0.99) or higher (**McCabe et al., 2001**).

2.10 Contacting Systems

There are two main different adsorption contacting systems:

2.10.1 Batch type Contacting System

Batch processes are important examples in which the adsorbent moves relative to the walls of the contaminated vessel. The simplest process involves a specific volume of wastewater is mixed with a quantity of adsorbent into a container until the pollutant in the solution has been decreased to desired level for a certain period of time, the concentration profiles decreases with time as shown in fig.(2-5) (**Levenspiel, 1962 & Suffet and McGuire, 1980**).



Batch reactor **Concentration-time profile**

Fig. (2-5) Schematic Illustration of the Experimental Batch Process

Where:

V: Volume of solute,

C_o: Initial concentration,

C_1: Concentration at given time.

2.10.2 Column-type (Continuous-flow) System

The aqueous solution with influent concentration flowed from the top to the bottom (fixed-bed) or from the bottom to the top (countercurrent moving bed) of the bed. The variation of the pollutant concentration in the water phase with time at different bed lengths can be measured.

Column-type operation appeared to have distinct advantage over the batch-type system. For column system the adsorbent is continuously in contact with fresh solution, consequently the concentration of the solution in contact with given layer of adsorbent in a column is relatively constant. For batch treatment the concentration of solute in contact with a specific quantity of adsorbent steadily decreases as adsorption proceeds, thereby decreasing the effectiveness of the adsorbent for removing the solute (**Weber, W. J., 1972**).

2.11 Selection of Experimental Conditions

2.11.1 Effect of Influent Concentration

The concentration of influent is one of the most important parameters that affect the adsorption process. It’s consider a (driving force) of mass transfer process of molecule from fluid phase to the solid phase. It was noted that with increasing influent concentration, the linear segment of the solute uptake curve extended over a shorter period of time (**Abu Regebaa, 1992**).

(**Weber and Keinath, 1967**) showed that the mass transfer rate for different organics increased with increasing the influent concentration.

(**Tan, I. A. W. et al., 2008**) prepared activated carbon from oil-palm shell, and studied the effect of variation in the initial influent concentration of MB dye used with the same adsorbent bed height and solution flow rate. They found that the breakpoint time decreased with increasing the inlet concentration and the adsorption capacity was increased with increasing the initial concentration because a high concentration difference provides a high driving force for the adsorption process.

2.11.2 Effect of Flow Rate

This effect is based on the assumption that film diffusion is rate limiting in early portion of column. Increasing the flow rate in this region may be expected to make a compression or reduction of the surface film. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate. Also, because the reduction in the surface film is due to disturbance created when the flow of the wastewater increased resulting of easy passage of pollutants through the particles and entering easily to the pores (**Abdul-Hammed, H. M., 1996**).

2.11.3 Effect of Bed Height

(**Tan, I. A. W. et al., 2008**) determined the breakthrough curve for MB adsorption on the activated carbon prepared from oil-palm shell at different bed heights and a constant flow rate of 20 ml/min and MB initial concentration of 100 mg/l. They found that both the breakthrough and exhaustion time increased with increasing the bed height.

(**Martin and Al-Bahrani, 1978**) showed that the service life of adsorbent column (carbon) increases with increasing bed depth and realized carbon adsorption capacity at break point increases at decreasing rate with increasing bed depth. This indicates that for deeper bed the contact time will increase.

2.11.4 Effect of Adsorbent Particle Size

In case of using an adsorbent particles of much smaller size, that will eliminate interparticle mass transfer resistance, so that the rate determining step is diffusion through film around each particle.

(**Malkoc and Nuhoglu, 2006**) worked on the sorption of Cr(VI) onto tea factory waste. The experiments were carried out using four different particle sizes 0.15-0.25, 0.25-0.5, 0.5-1 and 1-3 mm under constant flow rate, bed height and initial feed concentration. Smaller than average size particles can produce a delay of the breakthrough while larger than average particles, which approach equilibrium more slowly, can cause the opposite effect on the breakthrough curve. That is to say, in the finer particle size ranges, adsorption breakthrough curves followed a much more efficient profile than larger particle size ranges, in that the breakthrough time increased and the curve tends toward the classic S shaped profiles.

(**Walker and Weatherly, 1998**) showed that the rate of adsorption by small particles is controlled by the rate of mass transfer from the bulk fluid phase to the solid phase.

the breaking of larger particles tends to open tiny cracks and channels on the particle surface of the material resulting in more accessibility to better diffusion, owing to the smaller particle size (**Karthikeyan, G., et al., 2003**).

2.11.5 Effect of Temperature

The adsorption processes are exothermic. Thus adsorption rate will increase with decreasing temperature (**Alexander, P., 1981**).

Although of its exothermic reaction, it proceeds more rapidly at elevated temperature due to the increased diffusion of molecules into the fine pores of the carbon. The amount removed at equilibrium will however be lower at high temperature (**Alexander, P., 1981**).

(**Gurses, A., et al., 2005**) concluded in their study conducted on activated carbon produced from waste dogrose seeds, that the adsorption of methylene blue increases with increasing temperature.

2.11.6 Effect of pH

In general, adsorption process of pollutants from wastewater is increased with decreasing pH, since at low pH activated carbon is positively charged due to adsorption of hydrogen ion, while most colloids and all ionized polar groups on organic molecules are negatively charged (**Haidar, M., 1996**).

(**Yamin, Y., et al., 2007**) conducted a study to see the effect of the solution pH value on the adsorption of Methylene blue dye onto activated carbon. They found that the removal of methylene blue was increased with increasing pH of methylene blue aqueous solution. Lower adsorption of methylene blue at low pH is probably due to the presence of H^+ ions competing with the cations groups on the dye for adsorption sites. As surface charge density decrease with an increase in the solution pH, the electrostatic repulsion between the positively charged methylene blue and the surface of the activated carbon is lowered, this may result in an increase in the rate of adsorption.

CHAPTER THREE

EXPERIMENTAL WORK AND PROCEDURES

3.1 Materials

Materials used during the experimental work are the following:

3.1.1 Adsorbate

Methylene blue (MB) dye was chosen in this study because of its known strong adsorption onto solids, its recognized usefulness in characterizing adsorptive material (**Chongrak, K., et al., 1998**), and is often serves as a model compound for removing organic contaminants and colored bodies from aqueous solutions. Methylene blue which is the most commonly used material for dying cotton, wood, and silk, is a heterocyclic aromatic chemical compound with ($C_{16}H_{18}ClN_3S$, $3H_2O$) as molecular formula and a molecular weight of 373.9 x 10^{-3} kg mol^{-1} (**Hameed, et al., 2006**). The methylene blue used in present experimental work was supplied by the department of science of chemistry in Babylon University. The structure of methylene blue is given in Fig.(3-1), and some of its physical and chemical properties are shown in Table (3-1).

Methylene blue, a cationic dye, is not regarded as acutely toxic, but it has various harmful effects. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting and gastritis problems (**Haque et al., 2002; Ozer et al., 2007**).

Basic dyes have amino groups, or alkyl amino groups, as their auxochromes, and consequently have an overall positive charge. In other words, the coloured part of the molecule is the cation. Although the molecular charge is often shown on a specific atom in structural formula, it is the whole molecule that is charged (**Maximova, A. and Koumanova, B., 2007**).

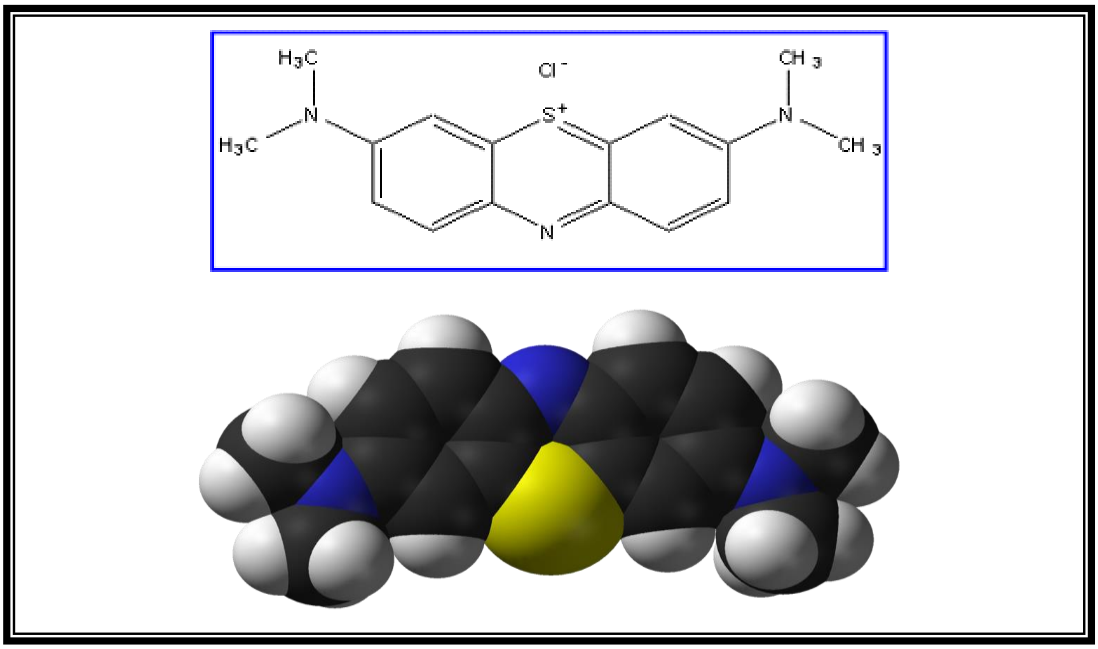


Fig.(3-1): Methylene Blue Structure (www.wikipedia.org)

Table (3-1): Some Physical Properties of Methylene Blue (MERCK, 2005)

Appearance	Physical state : solid Colour : dark-green, **Odour: odorless** Form : powder
Chemical name	3,7-bis(Dimethylamino)-phenazathionium chloride Tetramethylthionine chloride, trihydrate
Water solubility (g/l) at 20°C	40
Molecular weight (gm/mole)	373.9
Chemical formula	$C_{16}H_{18}ClN_3S.XH_2O$ (X=2-3)
Bulk density (Kg/m³)	400-600
Molecular diffusion (m²/s)	3.6×10^{-10}
Adsorption capacity	11-28 g/100g

3.1.2 Adsorbent

Three types of adsorbent were used in the present study:

1. Commercial activated carbon (GAC).
2. Activated carbon prepared from Iraqi Palm-date pits.
3. Iraqi siliceous rocks (Porcellanite).

3.1.2.1 Commercial Activated Carbon

The commercial activated carbon (GAC) with the physical properties listed in Table (3-2) was supplied by the Iraqi commercial markets. The mesh size of activated carbon used in the study was of (1mm). This size was obtained by sieving analysis using the American Sieve Standards in the building materials laboratory at the University of Babylon.

Table (3-2) Physical Properties of Activated Carbon Utilized in the Present Study (Commercial Markets)

Item name	Granular activated carbon
Base	Coconut shell
Bulk density	0.3×10^3 Kg/m^3
Particle density	1.5×10^3 Kg/m^3
BET surface area	650 m^2/g
Void fraction	0.4
Internal porosity	0.2
Ash content (%)	5 Max.
Iodine No. (mg/g)	1100-1130
pH	10.2-10.6

For pre-treatment, the activated carbon was firstly washed with distilled water and then dried in an electric oven at 120ºC overnight (**Yamin, et al., 2007**). This time was usually enough to remove any undesired moisture within the particles. It was then placed in desiccators for cooling.

3.1.2.2 Production of Palm-date Pits Activated Carbon

The preparation of activated carbon from the Iraqi palm-date pits was one of the main steps to achieve the objectives of the present study.

A. Palm-Date Pits

Date pits, also called pips, stones, kernels, or seeds form part of the integral date fruit in the order of, depending on variety and quality grade, 6-12% of its total weight, Fig.(3-2). Almost any organic matter with a large percentage of carbon could theoretically be activated to enhance its adsorptive characteristics (**Barreveld, 1993**). Table (3-3) shows that palm-date pits contain approximately 55-65% of carbohydrates. In view of this, high-grade activated carbon can be obtained from palm-date pits due to their high carbon content (Table 3-4) (**Al-Attas, O., 2003**).

Fig. (3-2) Date Pits Used in the Present Study

Table (3-3): Approximate Composition of Palm-date Pits (Barreveld, 1993)

Component	%
Moisture	5-10
Protein (N×6.25)	5-7
Oil	7-10
Crude fiber	10-20
Carbohydrates	55-65
Ash	1-2

Table (3-4): Summary of Major Components of Raw Palm-date Pits and Burned Palm-date Pits (Al-Attas, O., 2003).

Compounds	**Raw Palm-date Pits**		**Burned Palm-date Pits**	
	Phase	**Wt %**	**Phase**	**Wt %**
Amorphous Phase [C, O, H (Organic)]	Major	92	Major	88
Potassium Barium Phosphate Hydride [$KbaP_3O_9.H_2O$]	Minor	5	Minor	7
Potassium Hydroxide Hydride [$KOH.H_2O$]	Minor	2.5	Minor	3
Potassium Carbon Sulfur [K_2CS_2]	Minor	0.5	Minor	1.5
Hydrogen Phosphate [$H_4P_2O_7$]	Minor	-	Minor	0.5

B. Production of Activated Carbon from Iraqi Date Pits

This part of the study involves three steps for the production of activated carbon from Iraqi palm-date pits: boiling, soaking and a combined step of carbonization and activation of pits.

In the first step, the pits were initially boiled in a pressure cooker for about three hours at three stages with one hour interval for each stage. Boiling water was substituted with fresh water at the end of each interval. When the boiling duration was less than three hours, it was observed that the boiling water was of brown color. The boiling step was carried out in order to enhance the adsorption capacity of the pits during the soaking process. Before starting the second step, the boiled pits were dried in an electric oven at 110°C for 24 hours and then crushed with hammer. The resulting particles were sieved and the particles having a size of (1mm and 0.425mm) were used in the rest of the experimental work.

In the second step, which is soaking, the crushed pits were placed in glass containers. The two solutions commonly used in the chemical treatment process of producing activated carbon are Zinc Chloride ($ZnCl_2$) and Phosphoric Acid (H_3PO_4). Phosphoric acid was selected over zinc chloride because it is relatively safer than zinc chloride. During this step, a concentrated phosphoric acid (85% H_3PO_4) was poured carefully into the containers containing the pits with an impregnation ratio of (1 g of pits impregnated in 2 ml of 85% H_3PO_4) at 25 ºC (**Yağşi, N. U., 2004**) and an impregnation time of 24 hours. At the end of the soaking time, the soaked pits were left in air for partial dryness and then dried in an oven at 120ºC for one hour.

The final step adopted in this part of the study for the preparation of activated carbon from palm-date pits is the process of carbonization and activation. The date pits were placed on a metallic plate and subjected to an average temperature of 400°C (**Al-Attas, O., 2003**) for 2 hours. This heating period was selected based on the previous trials of different heating durations. From the various experimental trials performed, it was observed that when the heating duration was raised to more than 2 hours, the pits were completely carbonized to ash. After 2 hours of carbonization time, product was taken to a flask and distilled hot water was added. Then, Pits were washed with distilled boiling water until the desired pH was achieved (6.5), and then the product was dried in an electric oven at 120ºC overnight in order to remove any undesired moisture within the particles. The produced activated carbon is shown in Fig. (3-3).

Fig.(3-3) The Produced Activated Carbon

3.1.2.3 Iraqi Siliceous Rocks (Porcellanite)

The Porcellanite rocks used in this study were supplied by The General Establishment for Geological Survey and Mineralogy-Ministry of Industry and Minerals (GEGSM), from Akashat site in the western region of Iraq. These rocks were brought in a big stones form as shown in Fig. (3-4). The most pure white rocks were chosen to be used in the experiments.

Fig. (3-4) The Raw Porcellanite Rocks Used in the Present Study

As a pre-treatment, porcellanite rocks were crushed and sieved to get granular porcellanite with particle size of (1mm and 0.425mm) to be used in present experiments as shown in Fig.(3-5). The granular Porcellanite was then washed with distilled water and dried in an electrical oven at 120°C overnight. It was then placed in desiccators for cooling.

Fig. (3-5) Granular Porcellanite Used in the Present Study

3.2 Preparation of Samples with Different Date pits carbon-GAC Ratios

Different Palm-date pits AC-commercial activated carbon weight ratios were used starting from 0%, 10%, 12%, 15%, and 17% of date pits based activated carbon. The added palm-date pits activated carbon was with a size of 0.425mm while the size of GAC was of 1mm. Each sample was mixed by shaking using a shaker for 1 hour. The 10% ratio was first prepared and used in the experiments. when an increase in the operating time was achieved, the addition ratio was raised to 12% and so on until the operating time began to decrease.

3.3 Preparation of Samples with Different Porcellanite-GAC Ratios

The same procedure mentioned in section 3.2 was followed to prepare different Porcellanite-commercial activated carbon weight ratios starting from 0%, 10%, 12%, 15%, and 30% of porcellanite. The added porcellanite was with a size of 0.425mm while the size of GAC was of 1mm. A shaker was used to prepare the mixture of samples by shaking for 1 hour. The same strategy mentioned in section (3.2) was adopted in the selection of the different weight ratios of porcellanite.

3.4 Experimental Procedures

Tow types of experiments were carried out:

3.4.1 Equilibrium Isotherm Experiments

These experiments have been conducted to compare the adsorption behavior of both of the produced activated carbon (palm-date pits AC) and Iraqi porcellanite rocks with the adsorption behavior of commercial AC with respect to adsorption of methylene blue, and also to estimate the adsorption isotherm constants for the three adsorbents.

A stock solution of 100 mg/l of methylene blue (MB) was prepared for calibration purposes. From the stock, different concentrations of methylene blue were prepared by diluting with water. A spectrophotometer type (UV-1650 PC SHIMATZU) was used for the determination of absorbance at the predetermined maximum absorbance wavelength (λ_{max}=664 nm) of the MB dye for different concentrations of MB subsequently. λ_{max} was determined by performing a scan on a MB solution sample by the spectrophotometer, and the scan result chart is given in Appendix (A). A calibration curve of MB concentrations versus absorbency was constructed as shown in Appendix (A).

100 ml portions of MB solution of a 0.1 kg/m^3 concentration were placed in 6 conical flasks 250 ml in volume, containing different accurately weighed masses of commercial AC (0.4, 0.6, 0.8, 1, 1.2, and 1.4 gm) using an electrical four digits scale type (Sartorius BL 210S). Along with these flasks, one blank was also run. The whole set was then placed on a Wrist shaker for 24 hours at 25°C. After this period of shaking, samples were filtered using Whatmann No.1 filter paper, in order to minimize the interference of the carbon fines with the analysis, and the filtrates were analyzed for residual concentrations of MB using a double beam UV-visible spectrophotometer at a wavelength of 664 nm. The amount of adsorption at equilibrium, q_e (mg/mg), was calculated by the following equation (**Mahir et al., 2004**):

$$q_e = \frac{(C_O - C_e)V}{W} \qquad \text{……………………..…..(3-1)}$$

Where C_o and C_e (mg/l) are the liquid phase concentrations of dye at the initial and equilibrium conditions, respectively. V is the volume of the solution (l) and W is the mass of dry adsorbent used (mg).

In order to estimate equilibrium isotherms of the produced date pits AC and porcellanite, the same experiment mentioned above was repeated using the two materials respectively, and the results are given in Tables (4.1 to 3) in chapter four.

3.4.2 Fixed Bed Column Experiments

3.4.2.1 Experimental Arrangements

The schematic representation of experimental equipments is shown in Fig.(3-6). The pilot unit is depicted in Fig.(3-7).

3.4.2.2 Adsorption Column

Continuous flow adsorption studies were conducted in a glass column made of Pyrex glass tube of (0.8 m) height, and (0.05 m) internal diameter. The adsorbent bed was supported in the column by a fine porous stone, the influent solution was introduced to the column through a perforated plate, fixed at the top of the column to ensure a good distribution of the solution over the bed.

3.4.2.3 Feed Container

A 100 liter volume polyethylene cylindrical tank was used to prepare the feed solution.

3.4.2.4 Auxiliary Apparatus

(1) A 30 liter polyethylene container to collect the effluent solution.

(2) One calibrated rotameter type (Platon) was used to measure the flow rate ranged between (0.1 - 2) l/min.

(3) A centrifugal pump was used to feed the influent solution from feed container to the adsorption column. A part of solution was circulated to the feed container to achieve constant throuput.

(4) A (Q.V.F.) glass sampling valve was connected at the bottom end of the adsorber.

(5) Tow valves were used to control the desired flow rate through the adsorption column.

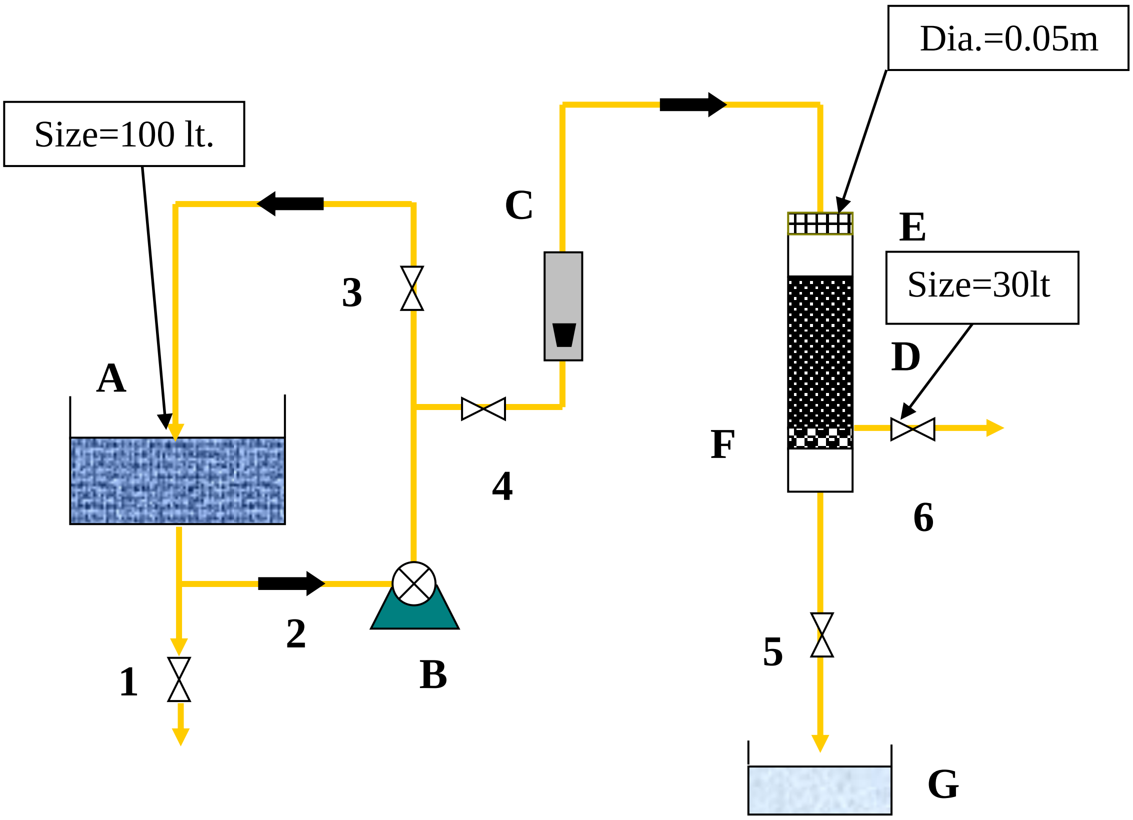


Fig. (3-6) Schematic Representation of Experimental Equipment

(A) Feed tank, (B) Pump, (C) Rotameter, (D) Packed bed adsorber

(E) Perforated plate, (F) Fine porous stone, (G) Effluent tank,

(1) Drain valve, (2) Pump valve, (3&4) Flow adjustment valves,

(5) Effluent valve, (6) Sampling valve

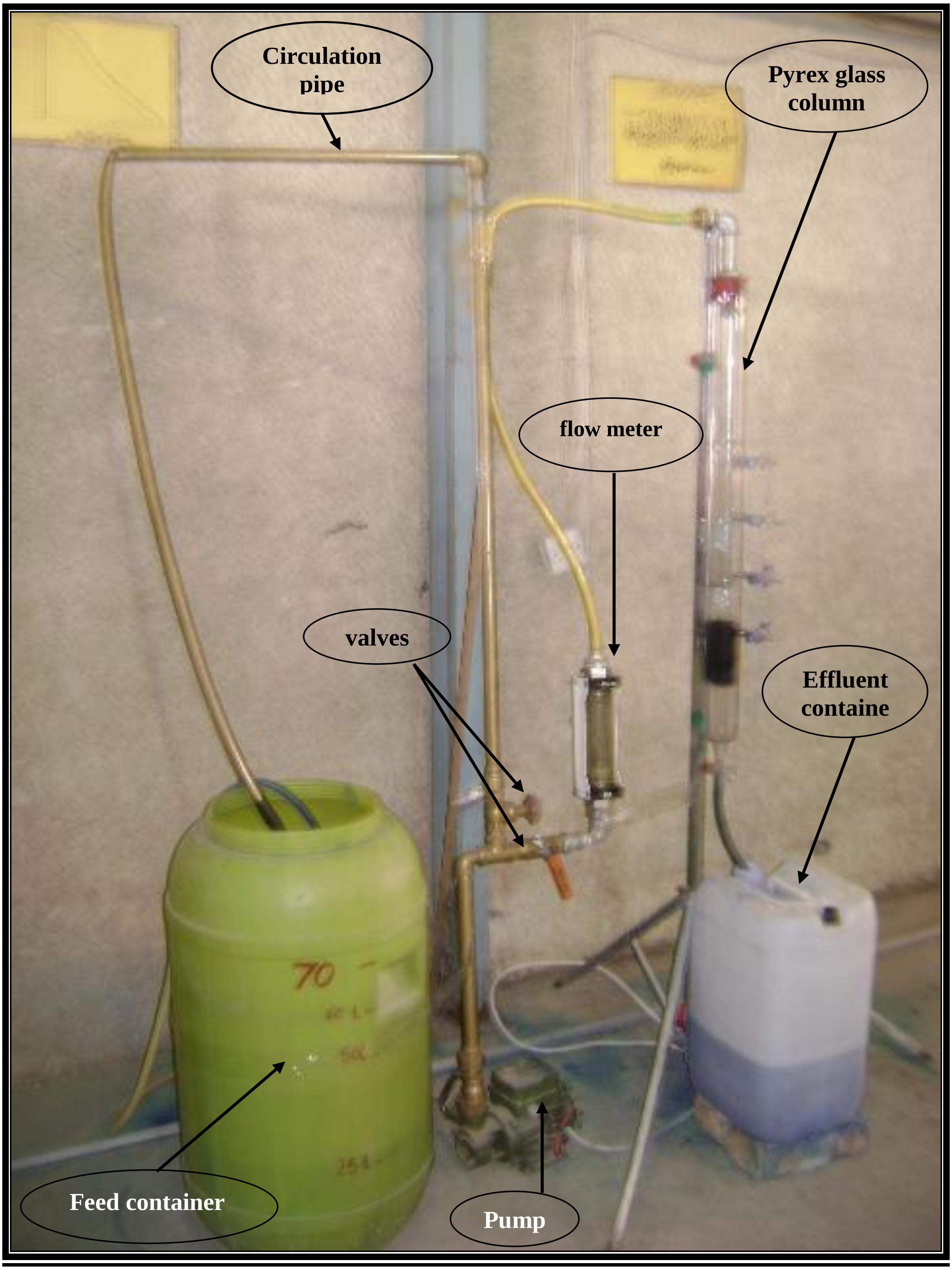


Fig. (3-7) General Arrangement of Pilot Unit

3.4.2.5 pH Control

The initial pH value of MB solution for all the experiments was adjusted to be 5 (**Ping and Guohua (I), 2001; Mohammed, A. M., 2006**). To achieve the pH of the influent of 5, a 38% concentration hydrochloric acid (HCL) was added gradually to the feed tank containing the MB solution, with a continuous agitation until the pH value of 5 was reached. The pH value was measured directly by using a calibrated pH meter. The pH meter was calibrated by means of buffer solution.

3.5 Analytical Technique

Due to the availability of UV Spectrophotometer device type (UV-1650 PC SHIMATZU) in the department of science of chemistry at the University of Babylon, it was used to measure the concentration of MB in samples. In this analytical technique, samples are used in solution and are placed in a small silica cell. Two lamps are used, a hydrogen deuterium lamp for the ultraviolet region and a tungsten/halogen lamp for the visible region. In this way radiation across the whole range is scanned by the spectrometer. A reference cell containing only solvent is used. Light is passed simultaneously through the sample cell and reference cell. The spectrometer compares the light passing through the sample with that passing through the reference cell. The transmitted radiation is detected and the spectrometer records the absorption spectrum by scanning the wavelength of the light passing through the cells.

3.6 Experimental Procedure

Column experiments were achieved to measure the breakthrough curve for MB dye. Three sets of experiments with seventeen experiments and different column systems were carried out at various adsorbent types, initial concentrations (C_O), flow rate (Q), bed depth (L), and different Date pits AC-GAC and Porcellanite-GAC weight ratios. All the experiments were carried out at room temperature (25±1°C), pH=5, and adsorbent particle size of

1mm, but in experiments of set No.3, the particle size of 0.425mm for both porcellanite and palm date-pits activated carbon was used while it was of 1mm for GAC.

All experimental conditions are summarized in Table (3-5). The experimental procedures for column system experiments were as follows:

(1) Using an electronic balance type (Sartorius BL 210S), an accurately weighed amount of the specific adsorbent was placed in the adsorption column to achieve the required bed depth.

(2) The MB solution with the desired concentration was prepared in feed container by dissolving a weighed amount of the powder MB dye in tap water.

(3) The MB solution pH value was adjusted to (5) using HCL acid.

(4) The solution was circulated via the centrifugal pump to achieve homogeneous solution.

(5) The MB solution was pumped to the adsorption column through the rotameter at the desired flow rate.

(6) Every (15) minutes at the beginning and then every (0.5) hour, a (3 ml) sample was taken from the outlet of the column and analyzed for MB concentration using UV Spectrophotometer until equilibrium state was reached. A photo of MB samples is shown in Fig. (3-8).

(7) The breakthrough curve was determined by plotting relating effluent concentration (C/C_O) against time. All results are given in Appendix (C).

Fig. (3-8) Samples of MB Solution

Table(3-5) Experimental Conditions of MB Adsorption onto Different Adsorbent Beds

Adsorbent	Bed depth, m	Flow rate, m³/sec	Concentration, Kg/m³	Particle size, m	date-pits		Porcellanite	
					%	Size, mm	%	Size, mm
Set No.1								
GAC	0.1	3.33×10^{-6}	0.05	1×10^{-3}	0	-	0	-
Date-pits AC	0.1	3.33×10^{-6}	0.05	1×10^{-3}	0	-	0	-
porcellanite	0.1	3.33×10^{-6}	0.05	1×10^{-3}	0	-	0	-
Set No.2								
GAC	0.05	3.33×10^{-6}	0.05	1×10^{-3}	0	-	0	-
GAC	0.1	3.33×10^{-6}	0.05	1×10^{-3}	0	-	0	-
GAC	0.15	3.33×10^{-6}	0.05	1×10^{-3}	0	-	0	-
GAC	0.1	3.33×10^{-6}	0.015	1×10^{-3}	0	-	0	-
GAC	0.1	3.33×10^{-6}	0.03	1×10^{-3}	0	-	0	-
GAC	0.1	2.2×10^{-6}	0.05	1×10^{-3}	0	-	0	-
GAC	0.1	4.17×10^{-6}	0.05	1×10^{-3}	0	-	0	-
Set No.3								
GAC	0.05	3.33×10^{-6}	0.05	1×10^{-3}	10	0.425		-
GAC	0.05	3.33×10^{-6}	0.05	1×10^{-3}	12	0.425		-
GAC	0.05	3.33×10^{-6}	0.05	1×10^{-3}	15	0.425		-
GAC	0.05	3.33×10^{-6}	0.05	1×10^{-3}	17	0.425		-
GAC	0.05	3.33×10^{-6}	0.05	1×10^{-3}	0	-		10
GAC	0.05	3.33×10^{-6}	0.05	1×10^{-3}	0	-		12
GAC	0.05	3.33×10^{-6}	0.05	1×10^{-3}	0	-		15
GAC	0.05	3.33×10^{-6}	0.05	1×10^{-3}	0	-		30

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

The adsorption of methylene blue dye onto three adsorbents that was used in the present study in fixed bed: commercial activated carbon (GAC), palm-date pits activated carbon, and porcellanite. They were studied using two types of experiments, batch and column experiments. Batch experiments were carried out to study the adsorption isotherm of methylene blue at 25±1°C and solution pH of (5) with different adsorbent dosages. Comparison was made to show the removal efficiencies by using different adsorbents. Equilibrium data were fitted to Langmuir and Freundlich models. The applicability of the isotherm equation to the adsorption study done was compared by judging the (R^2) values. Results of the batch study are given in Tables (C-1, C-2, and C-3) in Appendix C. Column experiments were carried out for studying the adsorption behavior of the fixed bed isothermal adsorber for the removal of methylene blue dye from water using different adsorbents (commercial activated carbon, palm-date pits activated carbon and Porcellanite). The effects of various initial dye concentrations, bed height, flow rate, (pits-GAC) ratio, and (Porcellanite-GAC) ratio for methylene blue adsorption on commercial activated carbon bed also were studied.

4.2 Batch Study

4.2.1 Estimation of the Adsorption Isotherm Constants for Commercial Activated Carbon System

The Langmuir, Freundlich, and the equilibrium adsorption isotherms of methylene blue adsorption onto commercial activated carbon of size (1mm) at 25±1°C and pH=5 are shown in figs.(4.1), (4.2) and (4.3) respectively. The obtained experimental data was correlated with Langmuir and Freundlich models which are illustrated in section (2.8). The parameters for each model were obtained from statistical regression of the obtained experimental data.

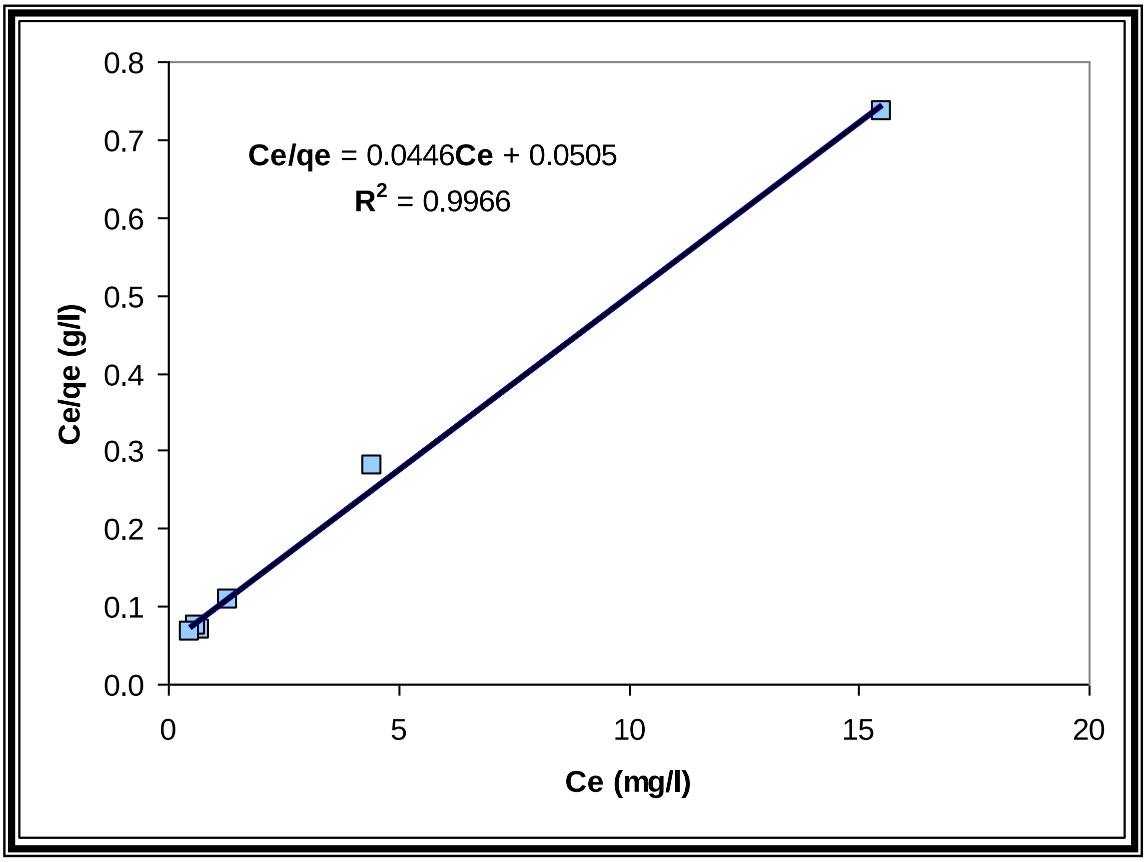


Fig.(4.1) Langmuir Adsorption Isotherm of Methylene Blue onto Commercial Carbon at 25±1°C, C_o=100 ppm and pH=5.

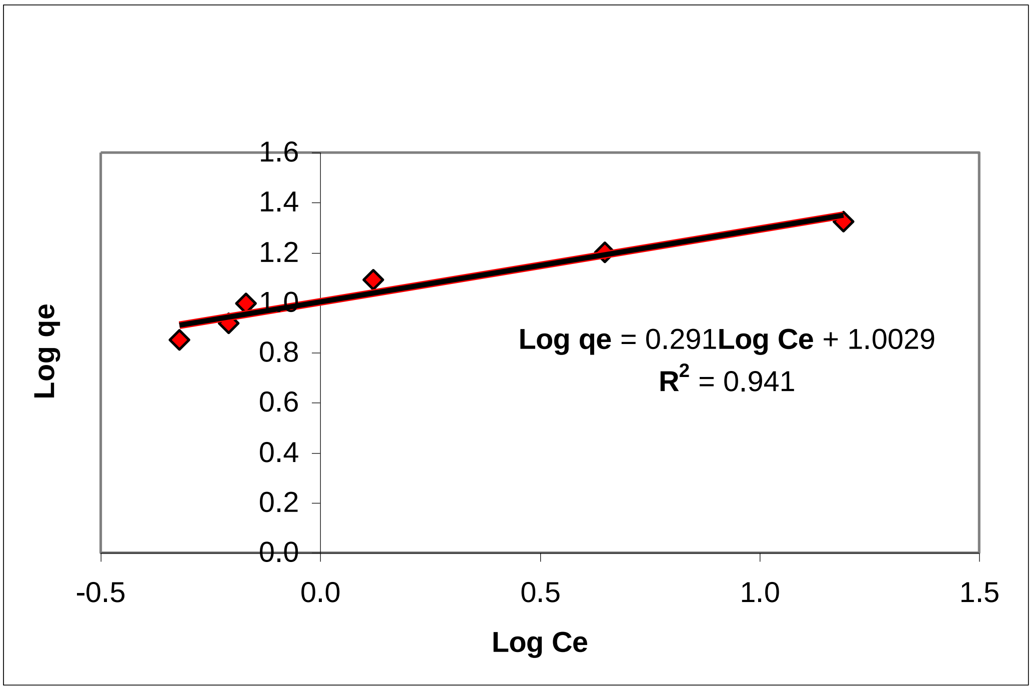


Fig. (4.2) Freundlich Adsorption Isotherm of Methylene Blue onto Commercial Carbon at 25±1 °C, Co=100 ppm, pH=5.

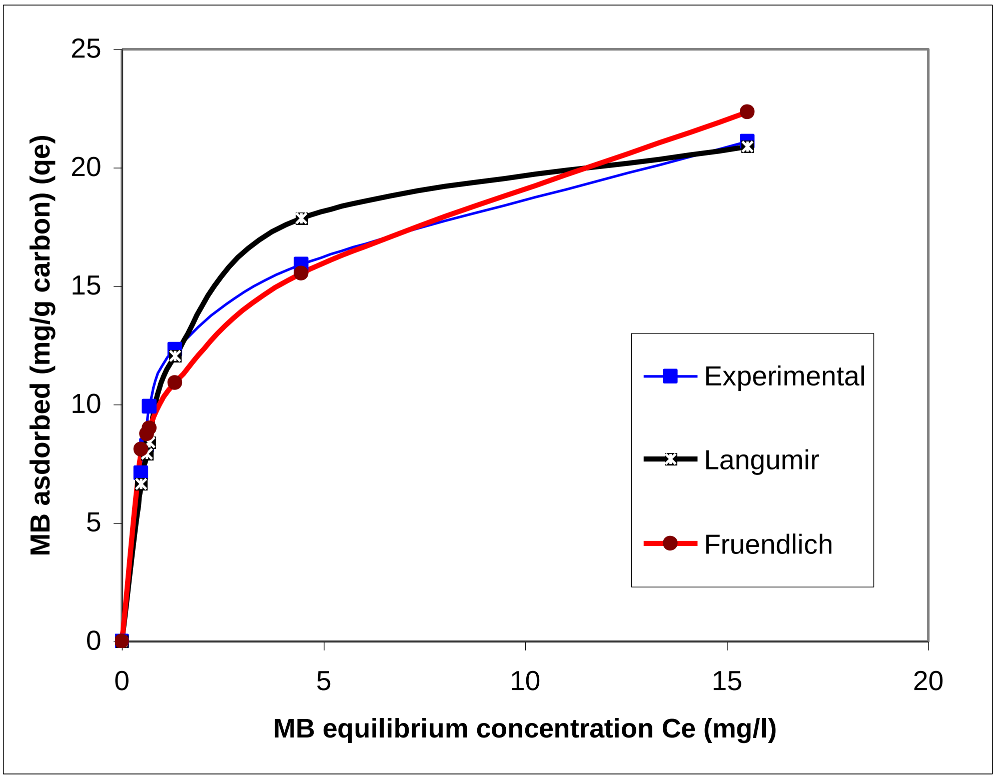


Fig.(4.3) Equilibrium Adsorption Isotherm of Methylene Blue Dye onto Commercial Carbon at 25±1 °C, Co=100 ppm, pH=5.

4.2.2 Estimation of the Adsorption Isotherm Constants for Palm-date Pits Activated Carbon System

The Langmuir, Freundlich, and the equilibrium adsorption isotherms of methylene blue adsorption onto the produced palm-date pits activated carbon of size (1mm) at 25±1°C are shown in figs. (4.4), (4.5) and (4.6) respectively. The obtained experimental data was correlated with Langmuir and Freundlich models which are illustrated in section (2.8). The parameters for each model were obtained from statistical regression of the obtained experimental data.

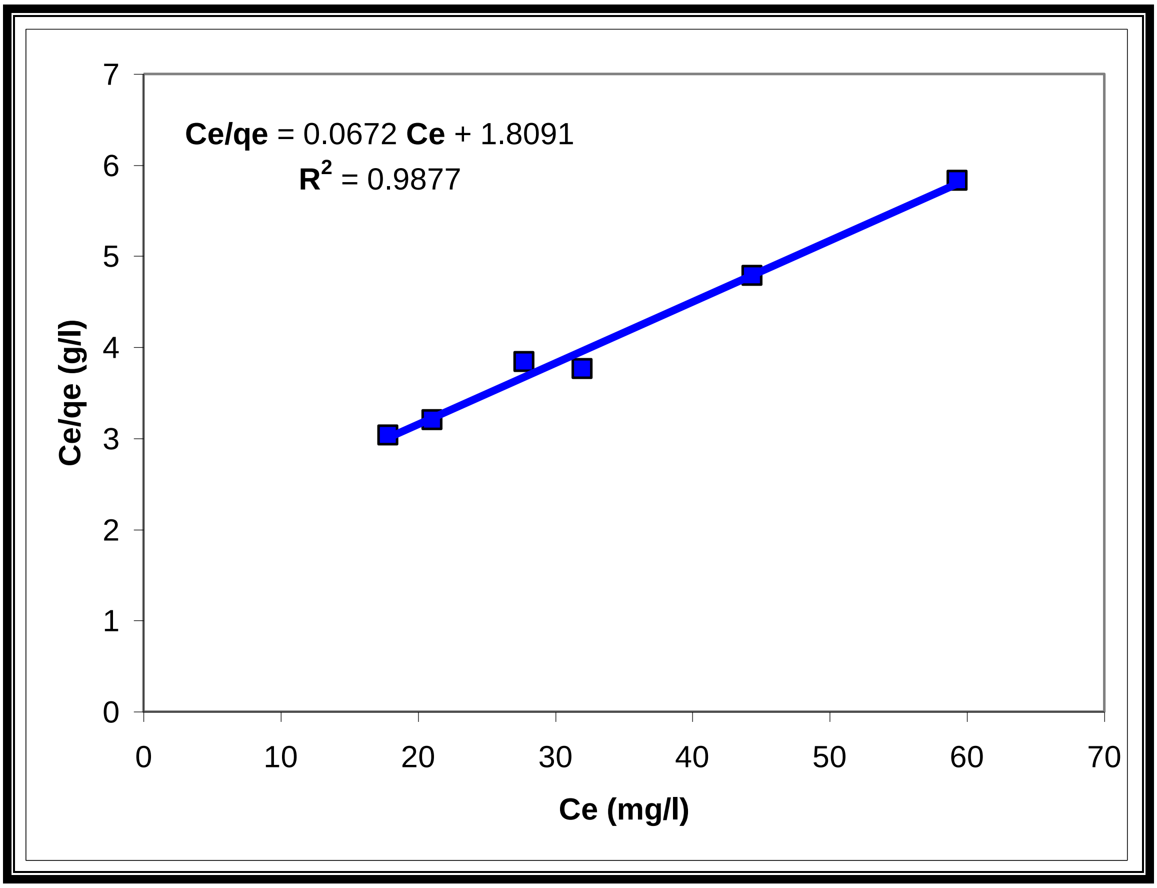


Fig.(4.4) Langmuir Adsorption Isotherm of Methylene Blue onto Palm-date Pits Carbon at 25±1 °C, C_O=100 ppm, pH=5.

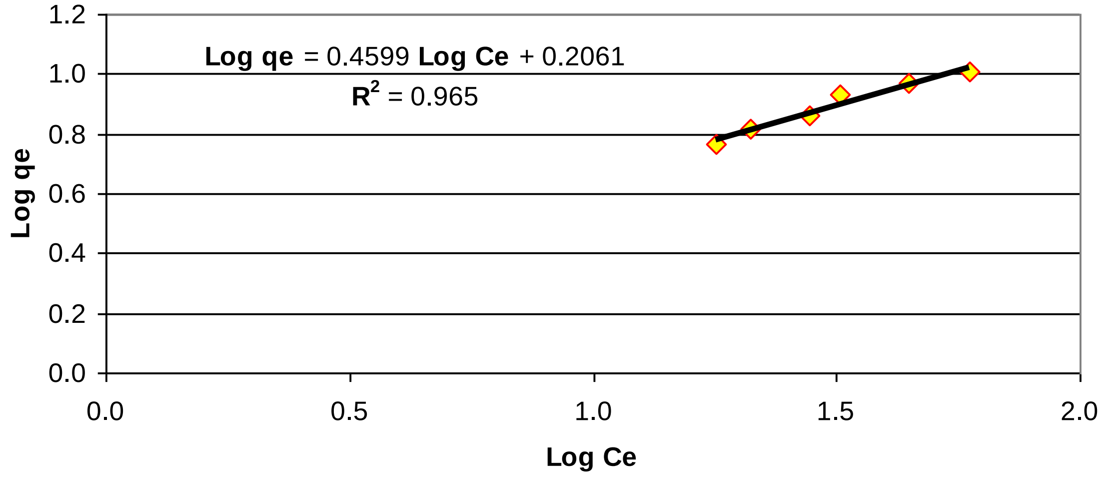


Fig.(4.5) Freundlich Adsorption isotherm of Methylene Blue onto Palm-date Pits Carbon at 25±1 °C, C_O=100 ppm, pH=5.

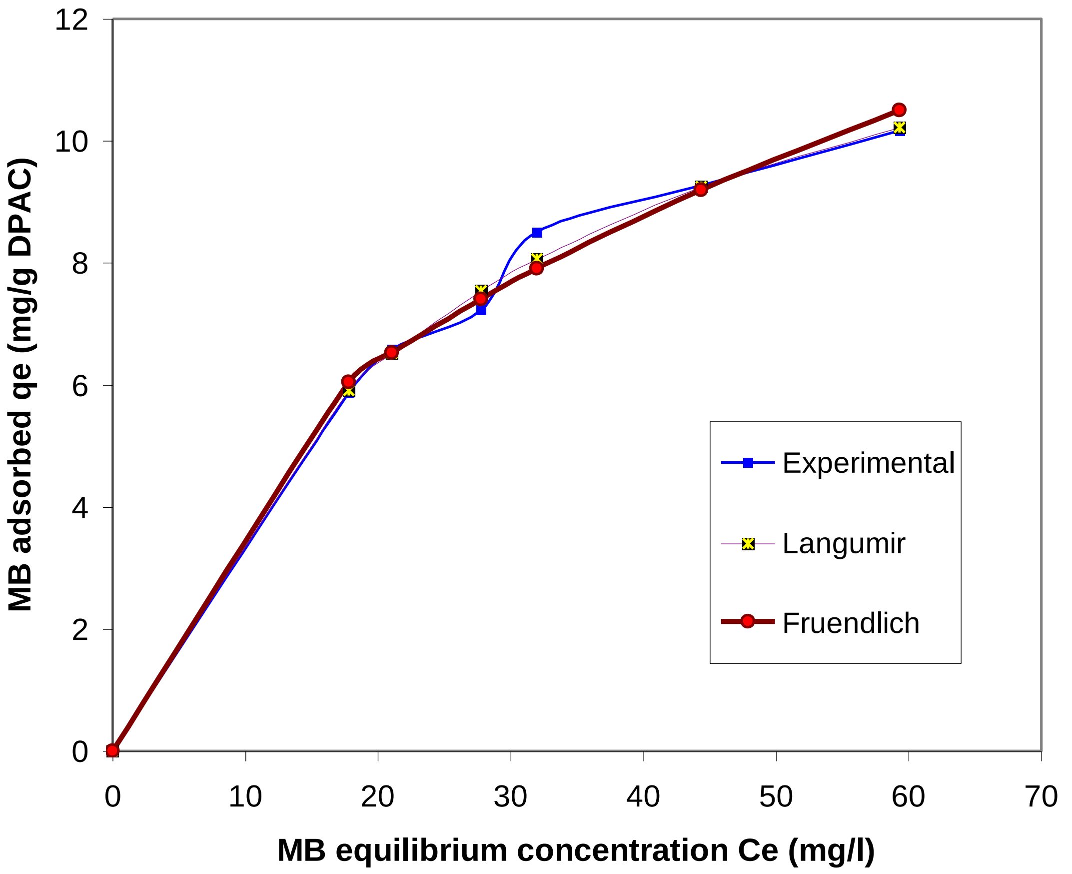


Fig.(4.6) Equilibrium Adsorption Isotherm of Methylene Blue Dye onto Palm-date Pits carbon at 25±1 °C, C_O=100 ppm, pH=5.

4.2.3 Estimation of the Adsorption Isotherm Constants for Porcellanite System

The Langmuir, Freundlich, and the equilibrium adsorption isotherms of methylene blue adsorption onto Porcellanite of size (1 mm) at 25±1 °C are shown in fig. (4.7), (4.8) and (4.9) respectively. The obtained experimental data was correlated with Langmuir and Freundlich models illustrated in section (2.8). The parameters for each model were obtained from statistical regression of the obtained experimental data.

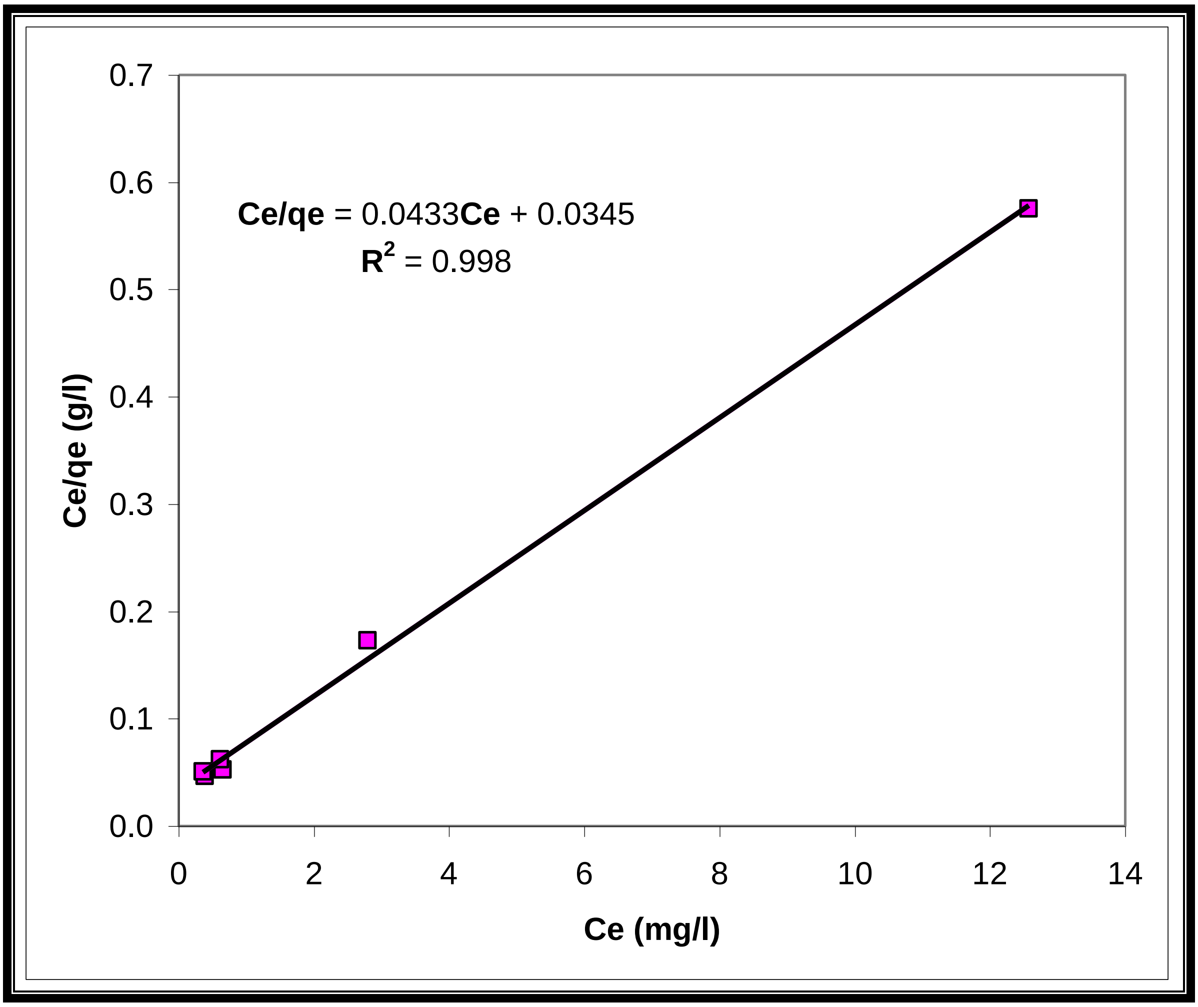


Fig.(4.7) Langmuir Adsorption Isotherm of Methylene Blue onto Porcellanite at 25±1°C, C_O=100 ppm, pH=5.

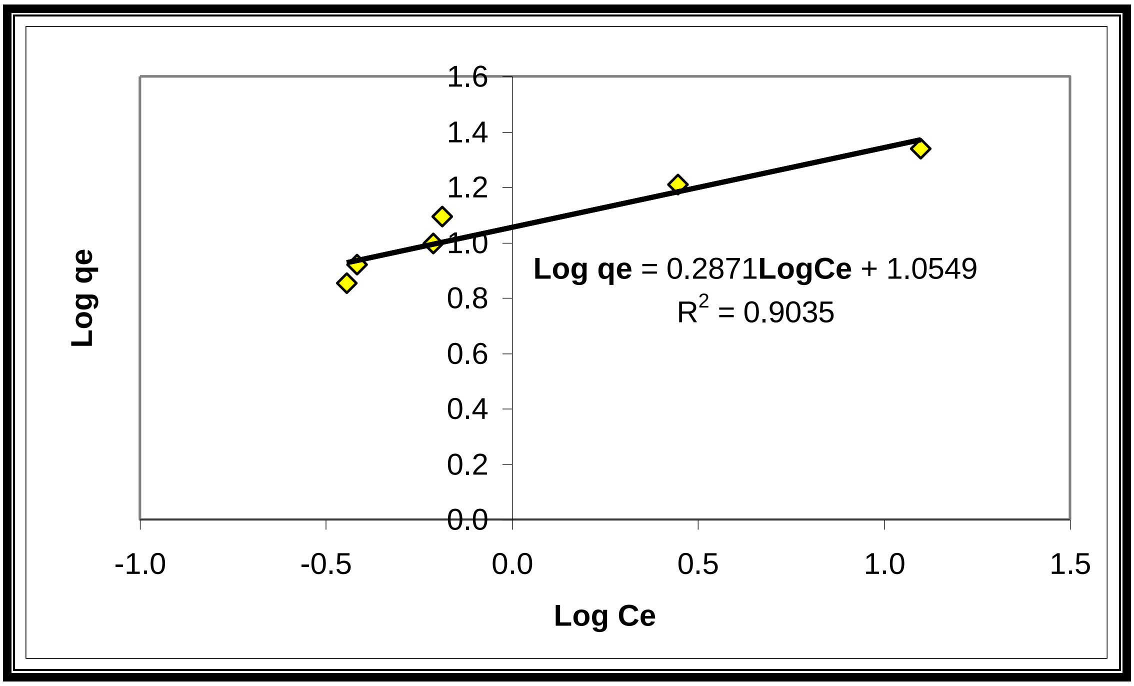


Fig.(4.8) Freundlich Adsorption Isotherm of Methylene Blue onto Porcellanite at 25±1°C, Co=100 ppm, pH=5.

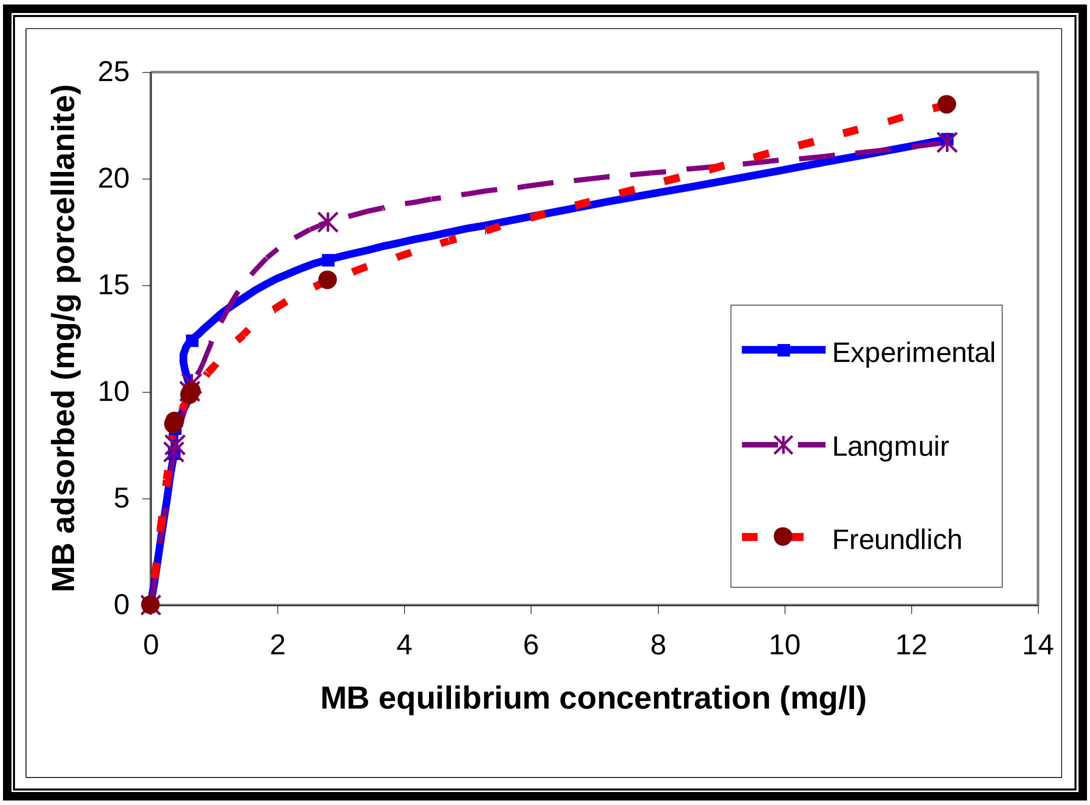


Fig.(4.9) Equilibrium Adsorption Isotherm of Methylene Blue Dye onto Porcellanite at 25±1°C, Co=100 ppm, pH=5.

In order to express the essential characteristics of the Langmuir isotherms, values of the dimensionless equilibrium parameter (R_L) were calculated using equation (2.5) illustrated in section (2.8). All parameters with their correlation coefficients for the three adsorbents are summarized in Table (4.1).

Table (4.1) Langmuir and Freundlich Isotherms Parameters for MB Adsorption onto Different Adsorbents Used in the Study.

Model	Adsorbent					
	Commercial AC		Date-pits AC		Porcellanite	
	Parameters	value	Parameters	value	Parameters	value
Langmuir (equation 2.3)	**Q_o, mg/g** **b, l/mg** R_L **Corr. Coeff.**	**22.42** **0.883** **0.0112** **0.9966**	**Q_o, mg/g** **b, l/mg** R_L **Corr. Coeff.**	**14.881** **0.037** **0.2128** **0.9877**	**Q_o, mg/g** **b, l/mg** R_L **Corr. Coeff.**	**23.095** **1.255** **0.0079** **0.998**
Freundlich (equation 2.1)	**K,mg/g(l/mg)$^{1/n}$** **n,** **Corr. Coeff.**	**10.067** **0.291** **0.941**	**K,mg/g(l/mg)1/n** **n,** **Corr. Coeff.**	**1.6073** **0.46** **0.965**	**K,mg/g(l/mg)1/n** **n,** **Corr. Coeff.**	**11.347** **0.287** **0.9035**

It is clear from the above figures and table that:

- The equilibrium isotherms for all the adsorbents used in the study are of favorable type, for being convex upward. These isotherms rise slightly at the initial stages for low C_e and q_e values. Eventually a plateau is reached in almost all the curves, indicating that the adsorbent is saturated at this level. The values of (R_L) also indicated that the Langmuir isotherms were favorable for adsorption of MB onto the three adsorbents used for being ($R_L<1$).
- In order to assess the different isotherms and their ability to correlate with experimental results, the correlation coefficient was employed to

ascertain the fit of each isotherm with experimental data. From table (4.1), the correlation coefficient values were higher for Langmuir than for Freundlich. This indicates that the Langmuir isotherm is clearly the better fitting isotherm to the experimental data. Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of the surfaces of the three adsorbents used, i.e. each dye molecule/adsorbent adsorption has equal adsorption activation energy. The results also demonstrate the formation of monolayer coverage of dye molecule at the outer surface of each adsorbent. Similar observation was reported by the adsorption of acid orange 10 dye onto activated carbons prepared from agricultural waste bagasse (**Tsai et al., 2001**), and by the adsorption of direct dyes on activated carbon prepared from sawdust (**Malik, 2004**), and adsorption of Congo red dye on activated carbon from coir pith (**Namasivayam, C. and Kavitha, D. 2002**).

- The equilibrium data for methylene blue adsorption on different adsorbents well fitted to the Langmuir equation, with maximum monolayer adsorption capacities of (21.86 mg/g), (21.12 mg/g), and (10.17 mg/g) exhibited by Porcellanite, commercial activated carbon and the produced activated carbon respectively. It is clear that Porcellanite is a very comparable material for the commercial activated carbon, while the adsorption capacity of the produced activated carbon was about half of that of porcellanite and commercial activated carbon under the same conditions of this study. Table (4.2) lists the comparison of maximum monolayer adsorption capacity of some dyes on various adsorbents (**Tan, et al., 2007**).

Table (4.2) Comparison of the Maximum Monolayer Adsorption of Some Dyes on Various Adsorbents (Tan, et al., 2007).

Dye	*Adsorbent*	*Maximum adsorption capacity (mg/g)*
MB	**Bamboo based Activated carbon**	454.2
MB	**Bamboo dust Activated carbon**	143.2
MB	**Groundnut shell Activated carbon**	164.9
MB	**Rice husk activated carbon**	343.5
Acid brown 283	**Sludge-based activated carbon**	20.5
Acid brown 283	**Chemviron GW activated carbon**	22
Direct red 89	**Chemviron GW activated carbon**	8.4
Direct black 168	**Chemviron GW activated carbon**	18.7
Congo red	**Coir-pith based activated carbon**	6.72

- From tables (C-1, C-2, and C-3) in Appendix C, it is evident that the produced activated carbon (date-pits based activated carbon) did not behave well in the removal of MB dye at low dosages as compared to Porcellanite and commercial carbon that achieved very high removal efficiencies at all dosages. At higher dosages (more than 0.8 g), the produced carbon started to achieve higher removal percentages of MB but the removal efficiency was still lower than that of porcellanite and commercial carbon. It can be concluded from the table that the produced carbon from palm-date pits can be used to remove methylene blue at higher dosages compared to porcellanite and commercial activated carbon.

- Porcellanite achieved very high removal efficiencies at all dosages, the matter which makes this natural material a competitive to the commercial activated carbon for the removal of methylene blue dye.

4.3 Column Experiments

The results of MB adsorption onto different adsorption fixed beds using a continuous system were presented in the form of breakthrough curves which showed the loading behaviors of MB to be adsorbed from the solution expressed in terms of relative concentration defined as the ratio of the outlet MB concentration to the inlet MB concentration as a function of time (C/C_o vs. time).

4.3.1 Breakthrough Curves of the Different Adsorbents

Three continuous flow adsorption experiments were conducted to study the adsorption behavior of fixed beds of commercial activated carbon, date-pits activated carbon and Porcellanite. All the experiments were conducted at constant conditions, bed depth (0.1m), initial MB concentration (0.05 Kg/m^3), flow rate (3.33×10^{-6} m^3/sec), particle size (1mm) and solution pH of (5). The breakthrough curves of the different adsorbents are presented in fig.(4.10) in terms of C/C_o versus time in minutes.

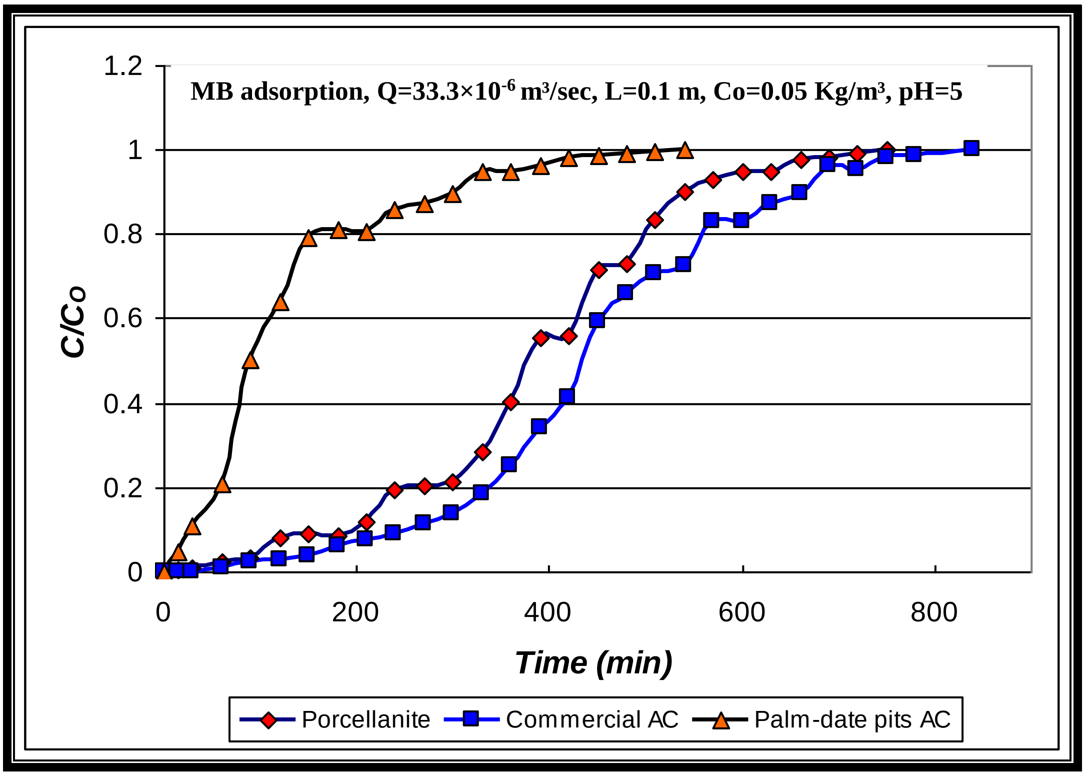


Fig.(4-10) Experimental Breakthrough Curves for MB Adsorption onto Different Types of Adsorbents at Constant Bed Depth, Flow Rate and Initial MB Concentration.

Fig.(4-10) shows that the three adsorbents that are used in the present study are efficient in the removal of methylene blue dye. The ranking of the three adsorbents in terms of operating time is commercial activated carbon (840 min.) > porcellanite (750 min.) > date-pits (540 min.). The use of porcellanite reduces the operating time by only 11% compared to the use of commercial activated carbon which makes this material very efficient candidate for the removal of methylene blue dye when taking to account that this material is cheap and locally available. The use of date-pits activated carbon reduces the operating time by 35% compared to commercial carbon. This can be attributed to the inefficient carbonization process which is carried out by using the available inefficient carbonization apparatus for the production of activated carbon from Iraqi date-pits. It is obvious from this figure that the breakthrough curves for all the adsorbents used are of S shape.

4.3.2 Effect of Initial Dye Concentration:

The effect of changing of initial dye concentration from 15 mg/l to 50 mg/l with constant bed height of commercial activated carbon of 10cm, flow rate of 3.33×10^{-6} m^3/sec, and solution pH of 5 is shown by the breakthrough curves presented in fig.(4-11). At the highest MB concentration of 50 mg/l, the activated carbon bed was exhausted in the shortest time of less than 14 hours leading to the earliest breakthrough. The breakpoint time decreased with increasing the initial concentration as the binding sites became more quickly saturated in the column. This indicated that an increase in the concentration could modify the adsorption rate through the bed. A decrease in the MB concentration gave an extended breakthrough curve indicating that a higher volume of the solution could be treated. This was due to the fact that a lower concentration gradient caused a slower transport due to a decrease in the diffusion coefficient or mass transfer coefficient. Similar trends were obtained for the adsorption of phenol by activated carbon (**Lin and Wang, 2002; Babu, 2004; Wa'adalla, 2006**).

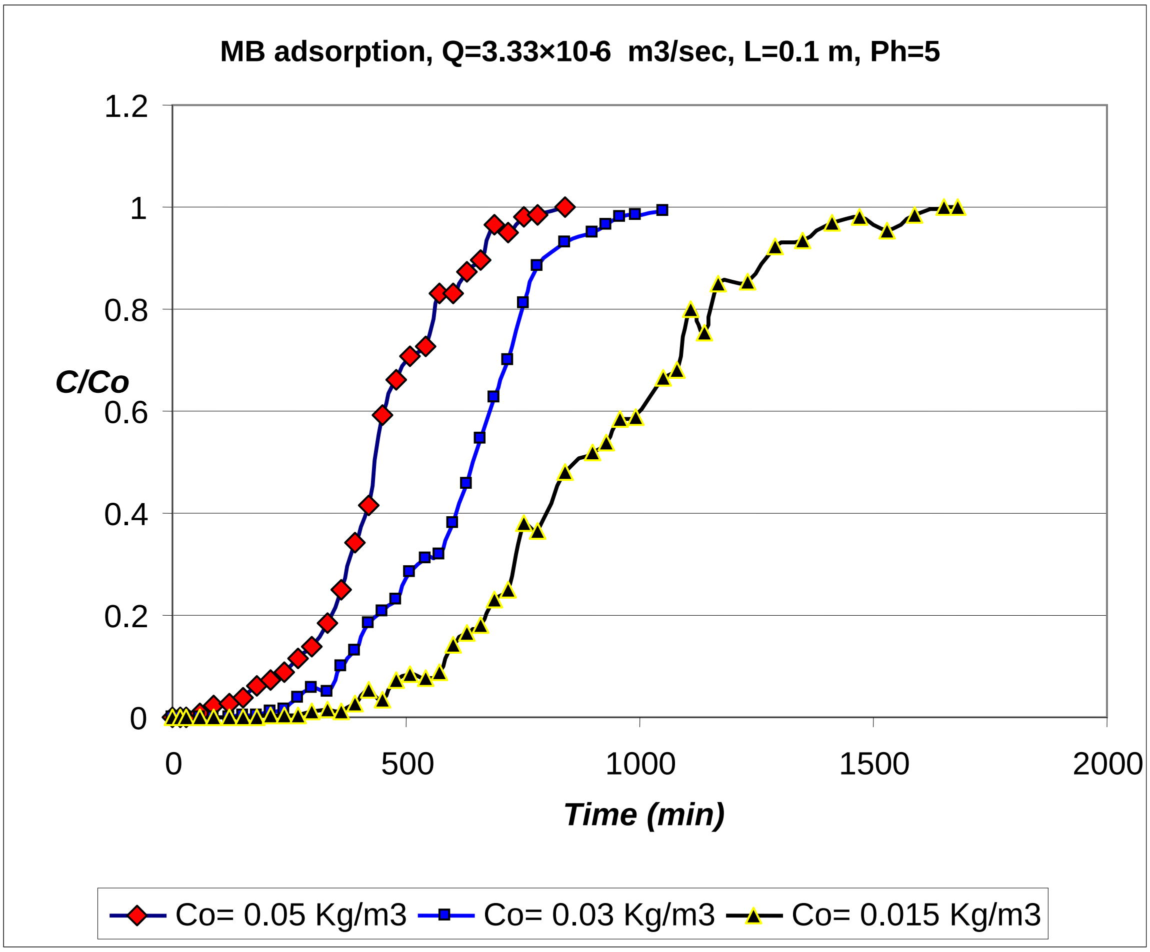


Fig.(4-11) Experimental Breakthrough Curves for MB Adsorption onto Commercial Activated Carbon at Different Initial MB Concentrations and Constant Bed Depth, and Flow Rate.

4.3.3 Effect of the Solution Flow Rate

The effect of the flow rate on the adsorption of MB using commercial activated carbon was investigated by varying the flow rate (2.2×10^{-6}, $3.33\times10^{-6,}$ and 4.17×10^{-6} m³/sec) with a constant carbon bed height of 10 cm, initial dye concentration of 50 mg/l, and solution pH of 5 as shown by the breakthrough curves in fig.(4-12).

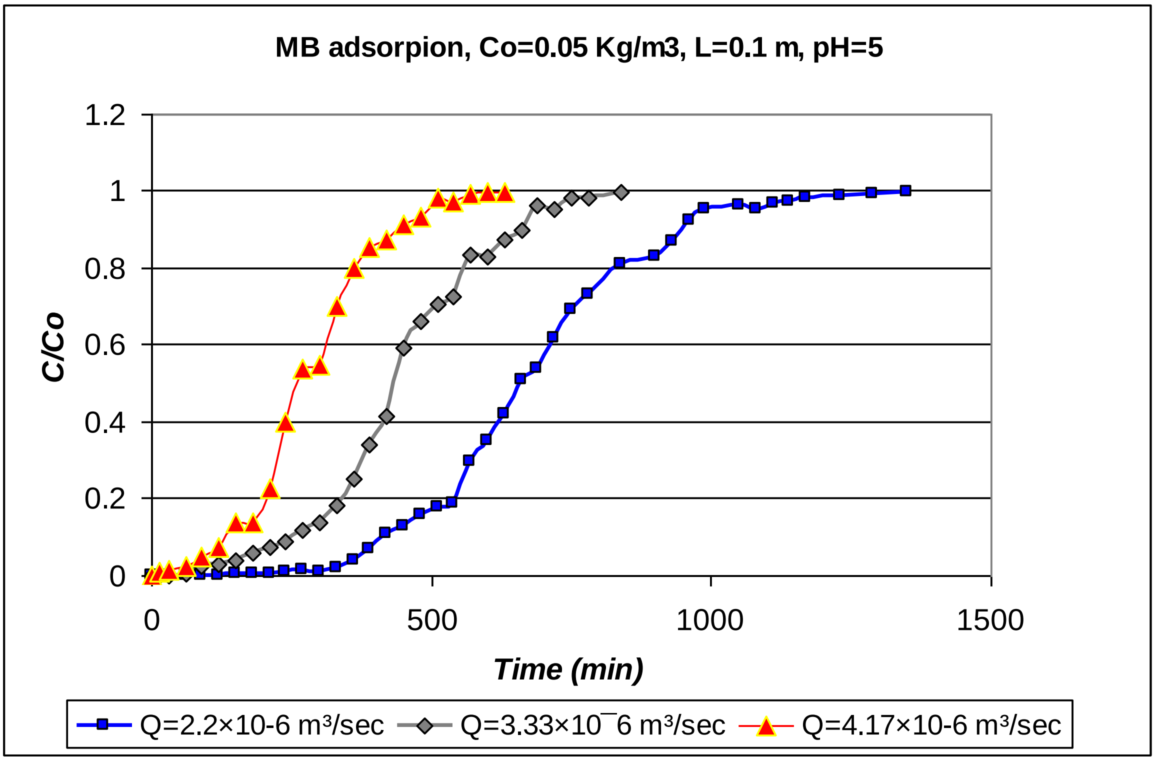


Fig.(4-12) Experimental Breakthrough Curves for MB Adsorption onto Commercial Activated Carbon at Different Flow Rates and Constant Initial MB Concentrations and Bed Depths.

Fig.(4.12) shows that as the flow rate increases from 2.2×10^{-6} m^3/sec to 3.33×10^{-6} m^3/sec to 4.17×10^{-6} m^3/sec, the breakpoint time decreases from 1350 min. to 840 min. to 630 min. respectively. Increasing the flow rate may be expected to make reduction of the surface film. Therefore; this will decrease the resistance to mass transfer and increase the mass transfer rate. The reduction in the surface film is due to the disturbance created when the flow of the feed increased. So, at a higher flow rate, the adsorption capacity was lower due to insufficient residence time of the solute in the column and diffusion of the solute into the pores of the adsorbent, and therefore, the solute left the column before equilibrium occurred. These results were in agreement with those reported in previous studies (**Walker and Weatherly, 1998; Gupta et al., 2001; Babu and Gupta, 2004; Waleed, 2004, Tan, et al., 2007, and Wa'adalla, 2006**).

4.3.4 Effect of Adsorbent Bed Height

Fig.(4-13) shows the breakthrough curves obtained for MB adsorption on the commercial activated carbon for three different bed heights of (5cm, 10cm, and 15cm), at a constant flow rate of 3.33×10^{-6} m³/sec, MB initial concentration of 50 mg/l, and solution pH of 5.

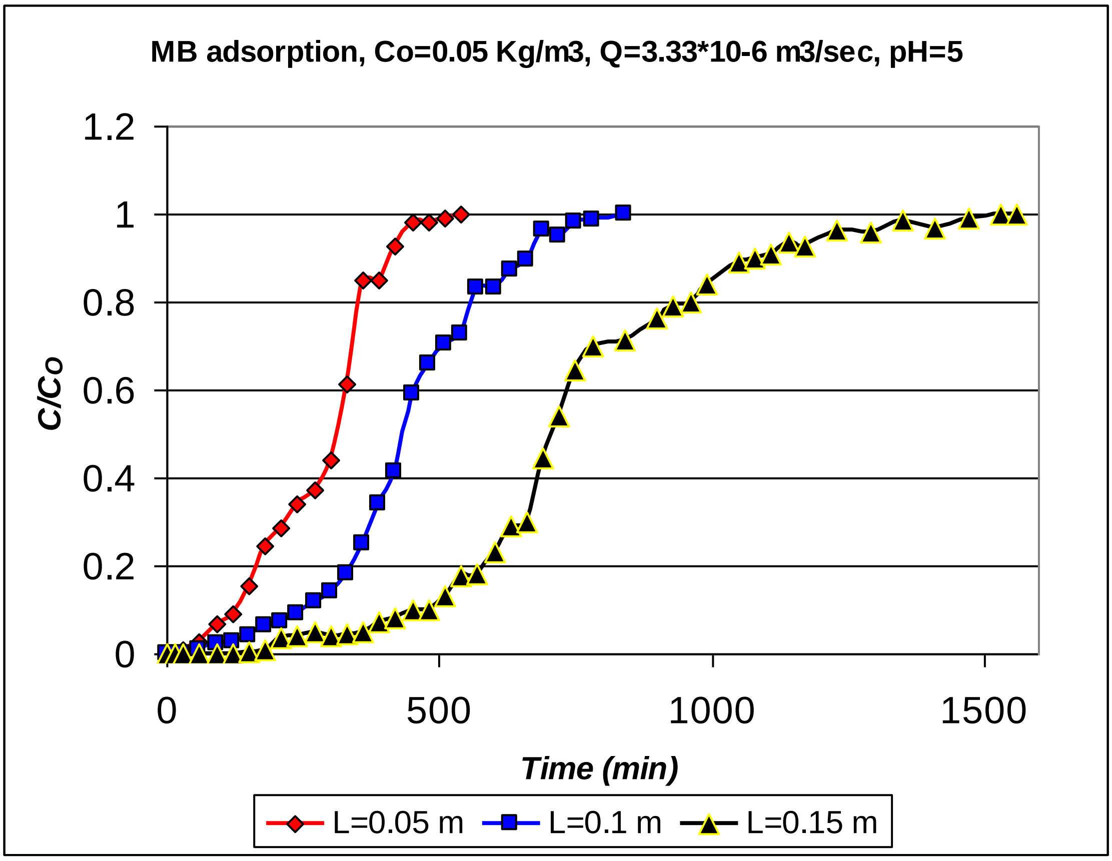


Fig.(4-13) Experimental Breakthrough Curves for MB Adsorption onto Commercial Activated Carbon at Different Bed Depths and Constant Flow Rates and Initial MB Concentrations.

Both the breakthrough and exhaustion time increased with increasing the bed height. A higher MB uptake was also expected at a higher bed height due to the increase in the specific surface of the activated carbon which provides more fixation binding sites for the dye to adsorb. The increase in the adsorbent mass in a higher bed provided a greater service area which would lead to an increase in the volume of the solution treated. (**Gupta et al., 2001, Waleed, 2004, and Wa'adalla, 2006**) reported in their works that when the bed height is reduced, axial dispersion phenomena predominates in the mass transfer and reduces the diffusion of the solute, and therefore, the solute has not enough time to diffuse into the whole of the adsorbent mass.

4.3.5 Effect of Different Porcellanite-GAC Ratios:

The effect of different Porcellanite-commercial AC weight ratios were investigated for MB adsorption onto commercial activated carbon by adding different weight ratios of (0.425mm particle size) porcellanite to the GAC bed which was of (1mm particle size). Five experiments were conducted using different weight ratios of (10%, 12%, 15%, and 30%) respectively. All experiments were carried out at constant flow rate, initial dye concentration, carbon bed height, and solution pH of (3.33×10^{-6} m^3/sec, 0.05 Kg/ m^3, 0.05m, and 5) respectively. The experimental breakthrough curves are presented in fig.(4-14).

Fig.(4-14) shows that a significant increase in the operating time is achieved by adding different ratios of porcellanite to activated carbon. Adding 10%, 12% and 15% porcellanite weight ratios to the activated carbon bed increases the operating time by 18%, 28% and 30% respectively.

Increasing the porcellanite ratio to 30% caused the operating time to decrease as compared to 10%, 12% and 15% ratios, but the bed was still achieving slightly higher operating time and removal efficiency than the pure (0% ratio) carbon bed.

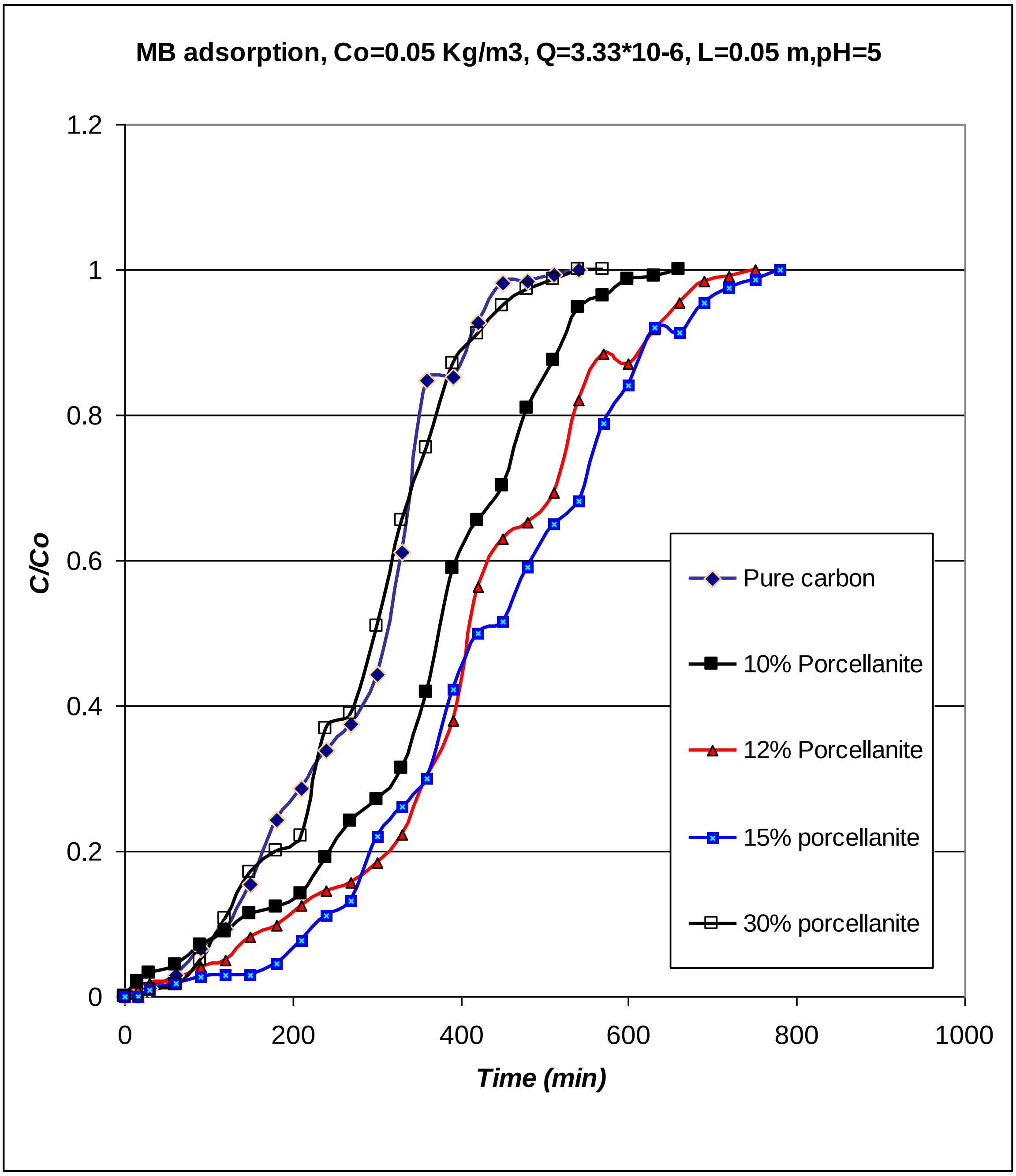


Fig.(4-14) Experimental Breakthrough Curves for MB Adsorption onto Commercial Activated Carbon at Different Porcellanite Ratios.

4.3.6 Effect of different palm-date pits AC-GAC ratios:

The effect of different date-pits AC/commercial AC weight ratios were investigated for MB adsorption onto commercial activated carbon by adding different weight ratios of (0.425mm particle size) date-pits carbon to the GAC bed which was of (1mm particle size. Five experiments were conducted using different weight ratios of (10%, 12%, 15%, and 17%) respectively. All experiments where carried out at constant flow rate, initial dye concentration, carbon bed height, and solution pH of (3.33×10^{-6} m^3/sec, 0.05 Kg/ m^3, 0.05m, and 5) respectively. The experimental breakthrough curves are presented in fig.(4-15).

It can be seen from this figure that adding 10% and 12% date-pits activated carbon to the commercial activated carbon bed increases the operating time of the bed by 10% and 22% respectively. It can be seen also that increasing the date-pits ratio to 15% and 17% reduces the operating time by 5% and 28% respectively and therefore makes the adsorption process not efficient compared with 0% date-pits ratio.

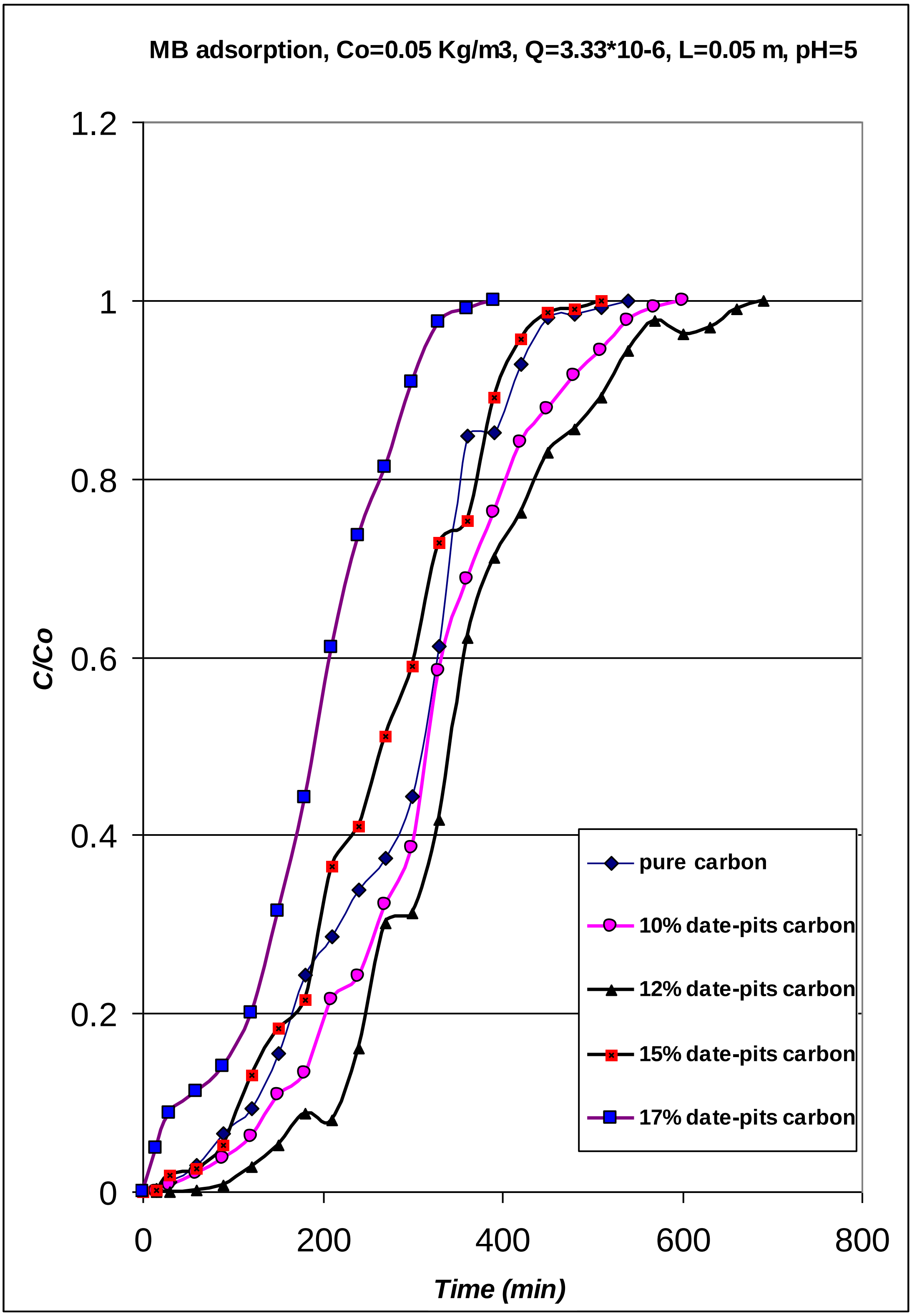


Fig.(4-15) Experimental Breakthrough Curves for MB Adsorption onto Commercial Activated Carbon at Different Iraqi Palm-date Pits Activated Carbon ratios.

4.4 Statistical Analysis

Multiple regression models were developed by using (Data Fit, version 9.0) program to simulate the experimental results shown in Table (4-3). These results were obtained by conducting several continuous flow experiments for the removal of MB dye by adsorption. Effects of flow rate, initial concentration, bed depth, porcellanite ratio, and date-pits carbon ratio were studied. The independent and dependent variables were selected as shown in Table (4-4).

Table (4-3) Experimental Column System Results

Exp. No.	Q (m^3/sec)	C_O (Kg/m^3)	Bed depth L, (m)	Date-pits%	Porcellanite (%)	Operating time, min.
1	3.33×10^{-6}	0.05	0.1	0	0	840
2	2.2×10^{-6}	0.05	0.1	0	0	1350
3	3.33×10^{-6}	0.05	0.15	0	0	1560
4	3.33×10^{-6}	0.015	0.1	0	0	1680
5	4.17×10^{-6}	0.05	0.1	0	0	630
6	3.33×10^{-6}	0.05	0.05	12	0	690
7	3.33×10^{-6}	0.05	0.05	17	0	390
8	3.33×10^{-6}	0.05	0.05	0	10	660
9	3.33×10^{-6}	0.05	0.05	0	15	780
10	3.33×10^{-6}	0.05	0.05	0	30	570

Table (4-4) Dependent and Independent Variables

Type	Variable	Description
Independent	X1	Flow rate (Q), in m³/sec
	X2	Initial concentration (C_O) in Kg/m³
	X3	Bed depth (L), in meter
	X4	Date pits ratio (DP), in percent
	X5	Porcellanite ratio (P), in percent
Dependent	y	Operating time (t), in minute

Three models were examined by using this program. These models with their symbols are shown in Table (4-5) below:

Table (4-5) Models Tested by Regression Analysis

No.	Model	Symbol
1	aX1+bX2+cX3+dX4+eX5+f	A
2	Exp(aX1+bX2+cX3+dX4+eX5+f)	B
3	aX1+bX2+cX3+dX4+eX5	C

4.4.1 Statistical Analysis Results

Statistical analysis results were obtained by applying Data Fit analysis on the experimental results given in Table (4-3). These results are shown in Tables below:

Table (4-6) Statistical Analysis Results (Governing Models)

Rank	Model	R^2
B	exp(aX1+bX2+cX3+dX4+eX5+f)	0.9476186644
A	aX1+bX2+cX3+dX4+eX5+f	0.9286464521
C	aX1+bX2+cX3+dX4+eX5	0.6305424102

From Table (4-6), it can be seen that model (B) represents the best model fits to the experimental data due to the higher R^2 value of (0.9476).

Table (4-7) Statistical Analysis Results (Regression Variable Results for Model B)

Variable	Value	Standard Error
a	-339760.516312409	107443.153272302
b	-16.6110726372051	3.63894288681893
c	9.32877074760085	2.4380652613443
d	-8.75578675102E-03	1.91686807447E-02
e	3.738788899161E-03	0.010682435907382
f	7.87424060651562	0.394496786138471

So, operating time can be given by the following equation:

$$\boxed{\mathbf{t}=\exp(-339760.5\mathbf{X1}-16.6\ \mathbf{X2}+9.328\ \mathbf{X3}-8.755\times10^{-3}\ \mathbf{X4}+3.74\times10^{-3}\ \mathbf{X5}+7.87)}$$

The above equation can be also written in terms of design parameters as the equation below, and the model plot is shown in fig.(4-16).

$$\boxed{\mathbf{t}=\exp(-339760.5\ \mathbf{Q}-16.6\ \mathbf{C_O}+9.328\ \mathbf{L}-8.755\times10^{-3}\ \mathbf{DP}+3.74\times10^{-3}\ \mathbf{P}+7.87)}$$

where:

t: is the operating time in (min).

Q: is the flow rate in (m^3/sec).

C_o: is the influent concentration in (Kg/m^3).

L: is the bed depth of adsorbent in (m).

DP: is the date-pits ratio added to activated carbon bed in percent.

P: is the porcellanite ratio added to activated carbon bed in percent.

It can be seen from Table (4-8) that the bed depth of the adsorbent has the most significant effect on the operating time of the fixed bed with a R^2

value of (0.755635). This can be attributed to the effect of the bed depth on the adsorbent mass available for adsorption, which provides a greater or smaller service area leading to significant effect on the operating time. Other parameters have different effects on the operating time with the sequence L > C_O > DP > Q > P as shown in Table (4-8).

Table (4-8) Statistical Analysis Results (Correlation Matrix of Data Analysis)

	Q	Co	L	DP	P	t
Q	1	-0.021756	-0.039359	0.032045	0.037376	-0.387135
Co	-0.021756	1	-0.201007	0.163653	0.190879	-0.60006
L	-0.039359	-0.201007	1	-0.444091	-0.517969	0.755635
DP	0.032045	0.163653	-0.444091	1	-0.281142	-0.463128
P	0.037376	0.190879	-0.517969	-0.281142	1	-0.365670
t	-0.387135	-0.60006	0.755635	-0.463128	-0.365670	1

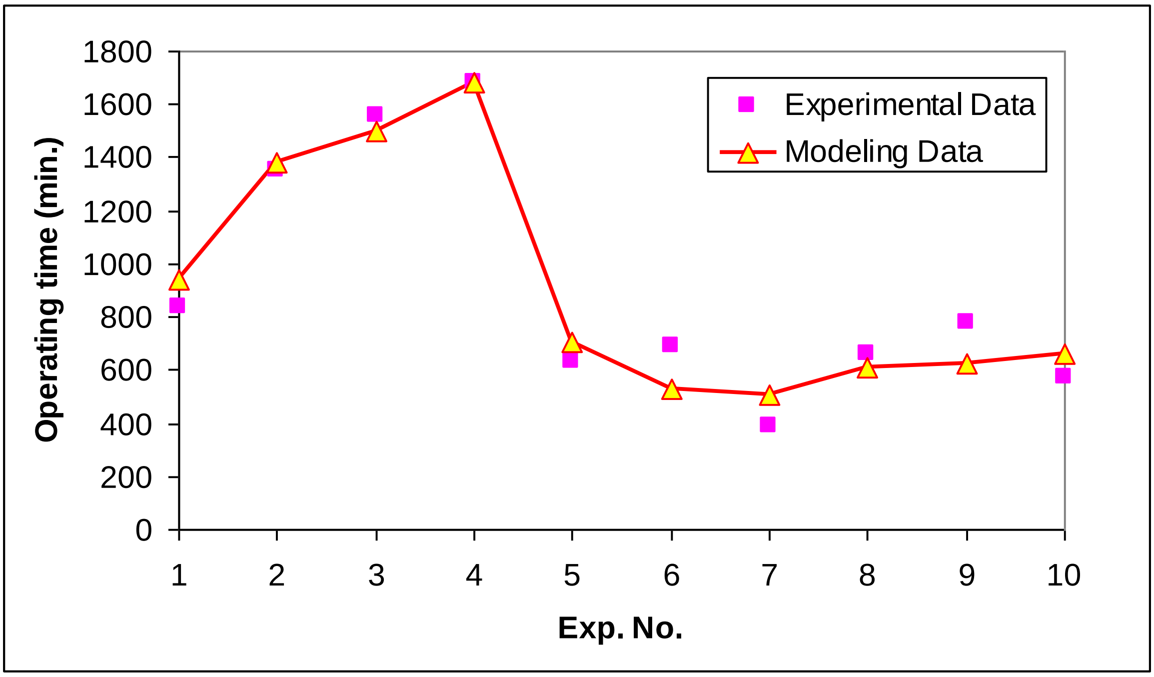


Fig.(4-16) Regression Model Plot

4.4.2 Verification and Calibration of Model

Verification for the obtained model can be made by plotting the experimental data which were not included in the building of the regression model versus modeling data. The obtained model was also calibrated by the following equation:

$Y = a X^b$

Where:

Y: Experimental Data

X: Modeling Data

a, b: Constants.

Verification of regression model is shown in Fig.(4-17). This fig. showed that the experimental data are correlated well with the modeling data.

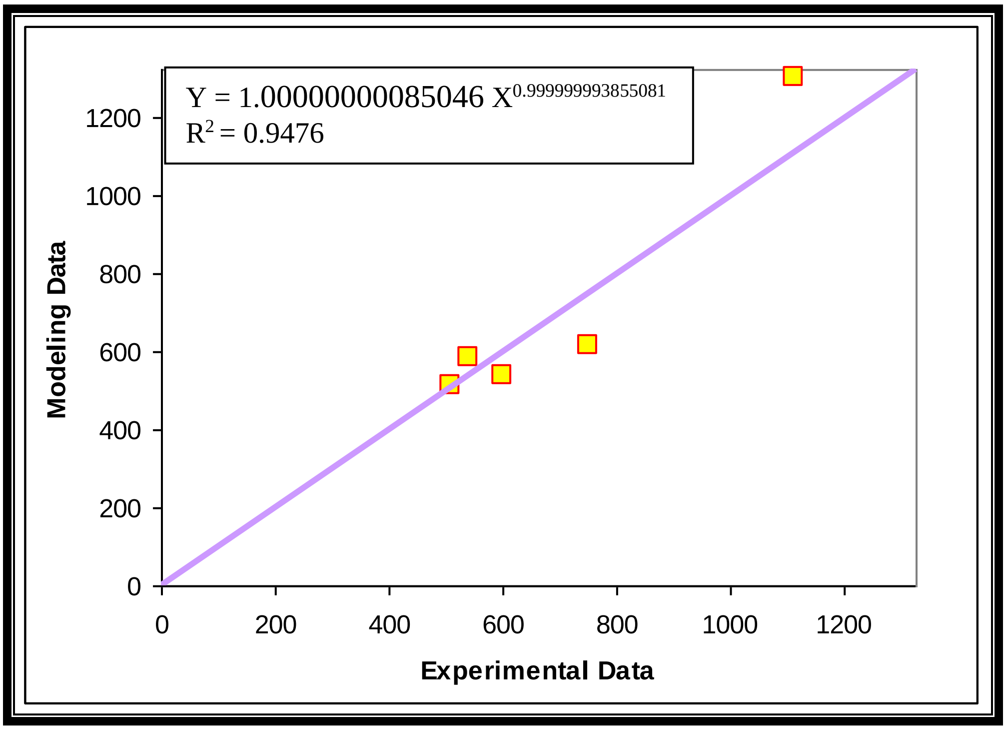


Fig.(4-17) Verification of Regression Model

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions are drawn from the present study based on the results discussed above:

1. The equilibrium isotherms for methylene blue adsorption onto the three adsorbents (GAC, date-pits activated carbon, and Porcellanite) used in present study are of favorable type. The obtained data of MB adsorption on the three adsorbents are correlated with Langmuir and Freundlich models and it is found that Langmuir model gives the best fit for the experimental data with very high coefficients of determination values.
2. Batch experiments show that the maximum adsorption capacity was achieved by porcellanite followed by commercial activated carbon and date-pits activated carbon with a very slight deference in adsorption capacity between porcellanite and commercial activated carbon.
3. Porcellanite and commercial activated carbon achieve very high removal efficiencies for methylene blue dye at all dosages, while the activated carbon produced from Iraqi palm-date pits achieve lower removal efficiencies at low dosages but its efficiency increases to 82.2% at the higher dosage used.
4. In continuous flow experiments, commercial activated carbon shows a slightly higher efficiency and about 11% longer operating

time than porcellanite and more higher efficiency and about 35% longer operating time than the date-pits activated carbon.

5. As the flow rate is increased, the breakthrough curve becomes steeper. The break point is reached earlier and effluent adsorbate concentration ratio (C/C_o) increases more rapidly due to the decrease in the contact time between the adsorbate and the adsorbent along the adsorption bed. For smaller bed height, (C/C_o) ratio increases more rapidly than for a higher bed height. For higher MB initial concentration, steeper breakthrough curves are obtained and break point is achieved sooner due to the increase in driving force for mass transfer.
6. Adding 10%, 12% and 15% of (0.425mm size) of porcellanite as weight ratios to the activated carbon bed increases the operating time by about 18%, 28% and 30% respectively due to the decrease in the dead zones between the carbon particles. And increasing the porcellanite ratio to 30% causes the operating time and removal efficiency to decrease as compared to 10%, 12% and 15% ratios. While adding 10% and 12% of (0.425mm size) of Iraqi date-pits activated carbon to the commercial activated carbon bed increases the operating time of the bed by about 10% and 22% respectively. Increasing the date-pits carbon ratio to 15% and 17% reduces the operating time by 5% and 28% respectively and therefore makes the adsorption process not efficient compared to 0% date-pits ratio.
7. The following correlation is obtained by applying multiple regression and represent the best fitting for the experimental data.

$$\mathbf{t}=\exp(-339760.5\mathbf{Q}-16.61\mathbf{C_o}+9.33\mathbf{L}-8.75\times10^{-3}\,\mathbf{DP}+3.74\times10^{-3}\,\mathbf{P}+7.87)$$

5.2 **Recommendations for Further Work**

Based on the results achieved in this study, the following recommendations can be forwarded:

1. Cycles and trials of producing activated carbon from Iraqi palm-date pits with high performance in adsorption must be conducted using another activation materials such Zink chloride or potassium hydroxide. It is also worthy investigating the production of palm-date pits activated carbon using steam activation.
2. Iraqi porcellanite rocks may be physically or chemically treated to enhance its adsorptive characteristics.
3. The produced activated carbon and porcellanite should be tested against different contaminants such as pesticides and heavy metals from either domestic or industrial waste water.