

# **Preparation and Characterization of Modified Activated Charcoal based on Ferula Communis and its Adsorptive Behavior**

**Jadir Nassir Abdulqadir**

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Approval of the Institute of Graduate Studies and Research

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Prof. Dr. Elvan Yilmaz  
Director

I certify that this thesis satisfies the requirements as a thesis for the degree of Master of Science in Chemistry.

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Prof. Dr. Mustafa Halilsoy  
Chair, Department of Chemistry

We certify that we have read this thesis and that in my opinion it is fully adequate in scope and quality as a thesis for the degree of Master of Science in Chemistry.

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Assoc. Prof. Dr. Mustafa Gazi  
Supervisor

Examining Committee

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1. Prof. Dr. Elvan Yilmaz

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2. Assoc. Prof. Dr. Mustafa Gazi

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3. Asst. Prof. Dr. Mehmet Garip

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## ABSTRACT

Activated carbon was prepared from *Ferula Communis* and chemically activated with phosphoric acid. The modified activated carbon was utilized for the removal of malachite green (MG) dye from simulated wastewater. Various operational parameters such as adsorbent dosage, solution pH, initial MG concentration and temperature were investigated. The results obtained were used to evaluate the adsorption isotherms and kinetics.

After analyzing experimental data, the sorption process of MG dye was favored to be pseudo-second order kinetic and the equilibrium data fitted the Langmuir isotherm. In addition, the data predicts that the adsorption process is controlled by chemisorption process. The maximum adsorption capacity was found at 298 K (239.9mg/g).

Activated carbon prepared from *Ferula Communis* can be an alternative precursor for commercial activated carbon production for the removal of dyes from industrial effluents.

Keywords: Activated Carbon. *Ferula Communis*, Malachite Green dye

## ÖZ

Bu çalışmada, Ferulla Communisin fosforik asit ile kimyasal aktivasyonu sonucunda aktif karbon hazırlanmıştır. Modifiye edilmiş aktif karbon, yapay atık sudan malachite green (MG) boyasının temizlenmesinde kullanılmıştır. Adsorbent kapasitesi için farklı boya başlangıç konsantrasyonu, adsorbent miktarı pH, sıcaklık, tuz varlığı ve etkileşim süreleri gibi farklı operasyon şartları incelenmiştir. Elde edilen sonuçlar adsorpsiyon izotermeleri ve kinetik değerlendirmelerinde kullanılmıştır.

Deneysel değerlerin analizi sonucunda MG boyasının tutunma prosesinin yalancı ikinci derece kinetiğe ve denge değerlerinin de Langmuir isoterme uyduğunu göstermektedir. Ek olarak, değerler adsorpsiyon prosesinin kimyasalsorplama prosesince kontrol edildiğini göstermiştir. Maksimum adsorpsiyon kapasitesi, 298 K' de 239.9 mg/g olarak bulunmuştur.

Ferula Communis'ten hazırlanan Aktif Karbon endüstriyel atıklardan boya arıtımı için ticari aktif karbon üretimi için alternative bir hammadde olabilir.

Anahtar Kelimeler: Aktif Karbon, Ferula Communis, Malachite Green dye, Bazik yeşil 4

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## **LIST OF SYMBOLS ABBREVIATIONS**

AC:	Activated Carbon
FCAC:	Ferula Communis Activated Carbon
STAC:	Spent Tea Leaves Activated Carbon
RPAC:	Rambutan Peel- Activated Carbon
RSC:	Borassus Aethipum Flowers Activated Carbon
MG:	Malachite Green
FT-IR:	Fourier Transform Infrared
UV/VIS:	Ultraviolet Visible
$R_L$ :	Equilibrium parameter Langmuir isotherm

# Chapter 1

## INTRODUCTION

Pollution is one of the significant problems the world is facing at the present time. It is not confined to the existence of human beings only but also affects the presence of all living organisms. Pollution can be divided into three types: air pollution, water pollution and contamination of the environment. Freshwater resources have been reduced as a result of industrial activities. Industrial activities are the main causes of pollution, especially organic materials produced from industries because they are non-biodegradable or do not degrade easily. Organic materials are commonly used in industrial processes such as dyes for application in paper production, textile, leather tanning, plastic and printing industries process. Dyes present in water reduce penetration of sunlight, causing a reduction in photosynthetic action thereby preventing the growth of the desirable aquatic life (Khambhaty et al, 2012).

Generally, dyes can be classified into (i) ionic dyes such as acid and reactive dyes, (ii) cationic dyes such as basic dyes, (iii) disperse dyes (Zümriye, 2005). Also, dye molecules consist of two main components; chromophores, which are responsible for color production and auxochromes which are responsible for the molecular solubility in water and promote affinity. In addition, auxochromes support chromophores (Suhas, 2009).

Malachite Green is one of the dyes that is mostly used heavily in the distilleries for the purposes of coloring. Also, it is used for dyeing of cotton; silk, paper and leather. Recent studies have shown that malachite green is linked to increased cancer risk due to its high cytotoxicity in mammalian cells, Carcinogenic, Mutagenic and Teratogenic effect on living organisms. IUPAC name of Malachite Green is [4-{[4-(dimethylamino)phenyl](phenyl)methylidene}-*N,N*-dimethylcyclohexa-2,5-dien-1-iminium chloride]. Molecular formula and molecular weight are  $C_{23}H_{25}ClN_2$ , and 364.91g/mole. The maximum adsorption of Malachite Green dye occurred at 618 nm.

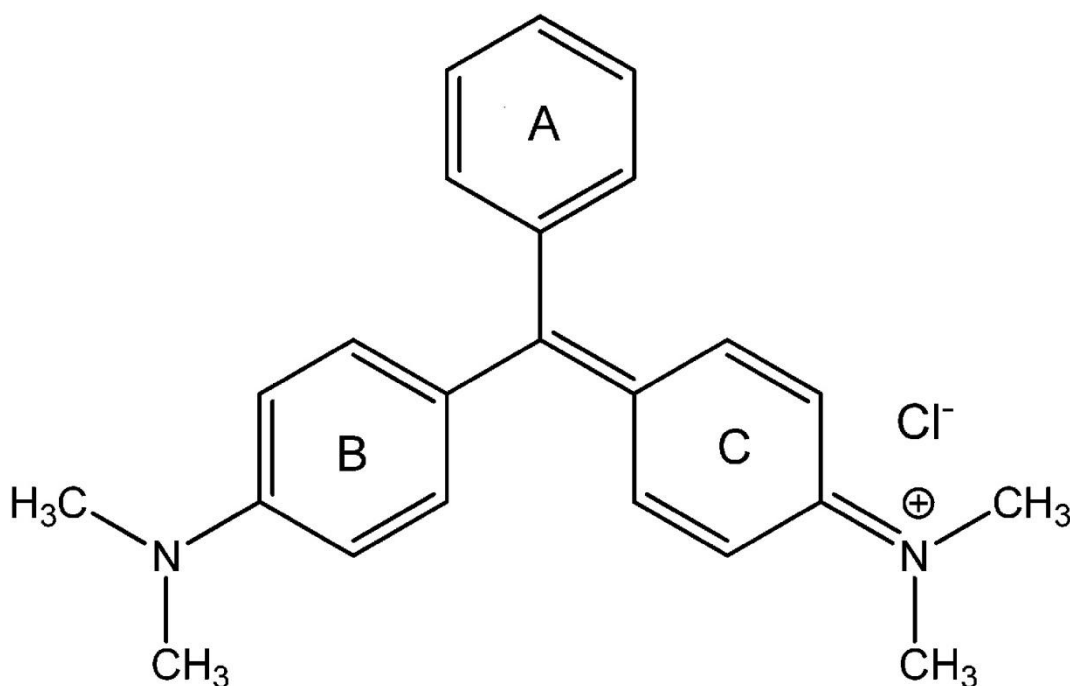


Figure 1-1: Chemical Structure of Malachite Green.

Various studies have been done using different adsorbent materials to remove malachite green from wastewater.

Adsorbents such as sugar cane dust, maize cob, rice-husk based active carbon, coal, fly ash and others have been proven as successful adsorbent materials for the removal of malachite green from aqueous solution (Akar et al, 2013). Diasa et al had reviewed various natural low cost waste materials as adsorbents to remove both metals and dyes in aqueous solution including Malachite Green (Diasa et al, 2007).

*Ferula communis* is an umbelliferous plant belonging to Apiaceae family. It is a perennial herb that commonly grows over six feet with showy yellow flowers. *Ferula Communis* is very close genera to anise and fennel. These plants are found in the center of western Asia, in the Mediterranean basin countries and extends to North of Africa including Cyprus (Zucca et al, 2013). This plant grows in mountainous area. Their life cycle starts from early spring, blooms in March and April and in June, it becomes dry. There are two chemo-types of *Ferula Communis*; poisonous and non-poisonous. Non-poisonous contains mostly daucane derivatives. Goats ingest fresh branches, leaves and flocks grazed it with other herbaceous vegetation (Seki et al, 2013). Different chemical investigations have reported the presence of ducanes esters and phenylpropanoid compounds in fruits and roots of *Ferula Communis*. In traditional pharmacopoeia, several species of this genus were used as tranquilizers and for the treatments of digestive disorders, rheumatism, headache, arthritis, dizziness and toothache. Als, it was used as a treatment for diabetes and exhibits antimicrobial properties (Mamoci et al. 2012).



Figure 1-2: Ferula Communis Plant

Present research work is aimed at producing efficient and low cost adsorbent from green plant source namely Ferula Cummonis for removing colors from wastewater treatment. Various adsorption parameters were evaluated to elucidate the efficiency of the prepared adsorbent.

### **1.1 Definition and Properties**

Activated carbon, also known as activated charcoal, is a form of carbon that is composed of a group of materials including a wide range of carboneous materials known for its small sized pores and high surface area that ranges from 100-1500  $\text{m}^2/\text{g}$  (Kilic et al, 2012). The main properties of activated carbons include high surface area, microcrystalline structures, high thermostability, low acid-base reactivity, high performance, high degree of surface reactivity and wide pore size distribution. These properties make activated carbon a unique and versatile material.

In the last decades, activated carbon acquired much attention in different technologies, especially in adsorption processes (Williams & Reed, 2006). Also activated carbon is stable to light, heat and many oxidizing agent due to its complex molecular structures (Khambhaty et al, 2012). Therefore, activated carbon is preferred as adsorbent for adsorption. There are five forms of activated carbon including granular, powders, extrudates, fibers and beads forms. The most preferred form of activated carbon for adsorption process in aqueous solution is the granular form because it can be separated from aqueous solution easily without any purification process. But the powder form requires separation from the solution. In addition, both granular and powder form can be used in gaseous phase (Yeganeh et al, 2006).



Figure 1-3: Granular Form of Activated Carbon.

### **1.1.1 Physical Structure of Activated Carbon**

In 1950, Franklin studied the structure of carbonized materials and noticed two different well defined types: non-graphitizing carbon and graphitizing carbon. These differences in structure are obvious from the earliest stages of carbonization, and may be attributed essentially to the formation at low temperatures (Zhao et al, 2009).

Generally, the substances that have high ratio of oxygen or low ratio of hydrogen content are called non-graphitizing carbon. The non-graphitizing carbons demonstrate a strong order of cross linking of crystallites during heating at low temperature, forming a porous carbon. This leads to a random orientation of the crystallites in a rigid, finely porous mass. Activated carbons were derived from non-graphitizing carbon (Franklin, 1951), meaning that it cannot be transformed into crystalline graphite even at temperature of 3000 °C. The neutron diffraction studies showed that non-graphitizing carbons consist entirely of  $sp^2$  atoms. The structures of non-graphitizing carbon were related to that of fullerenes (Harris et al, 2008). Such structures could explain the micro-porosity of the carbon and many of its other properties. The crystallite growth is impeded both by the strong cross-linking between neighboring crystallites and by their random orientation (Franklin, 1951). While, substances that have high ratio of hydrogen or low ratio of oxygen contents are called graphitizing carbon. During early stages of carbonization the crystallites remain comparatively unstable making it much weaker in cross linking (Harris et al, 2008). The structure is more impact and neighboring crystallites have a strong tendency to lie in nearly parallel orientation. The crystallite growth in graphitizing carbon occurs by the gradual displacement of whole layer-planes or even of groups of layer-planes. The pre-orientation existing in the graphitizing carbons facilitates



this process, enabling the rearrangement of the layer-planes to take place by small stages (Franklin, 1951).

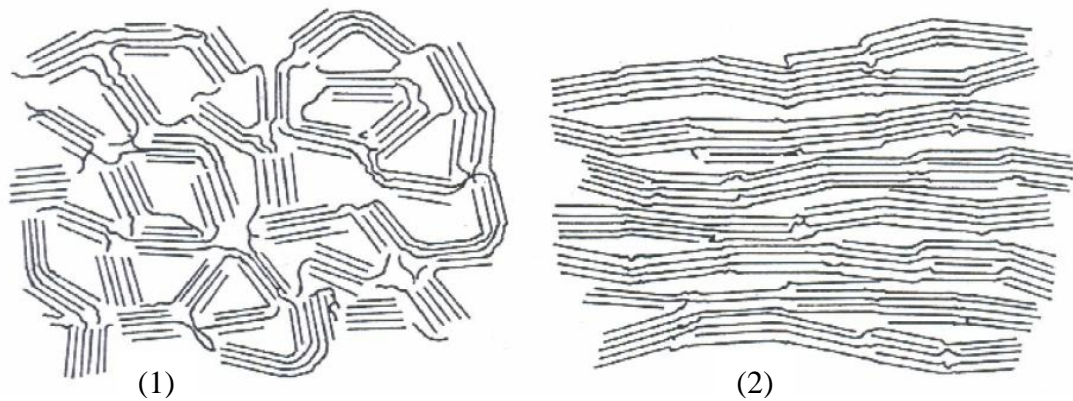


Figure 1- 4: Schematic Representation of (1) Non-graphitizing And (2) Graphitizing Structure Of Carbon.

Activated carbon is much closer to graphite in properties and structure. Graphite is composed of layers of fused hexagons held by weak Van der Waals force. These layers are held by carbon-carbon bonds (Harris et al, 2008). Regarding the structures, interlayer spacing in graphite is 0.335nm. Activated carbon is a muddled form of graphite, as a result of the presence of impurities and the activation process. The interlayer space in activated carbon ranges between 0.34nm and 0.35nm. Activation temperatures and carbonization produced more enhanced structure. Regarding the pore structures, it can be divided into three types: Micropores having a diameter less than 100 Angstroms. Mesopores is between 100-1000 Angstroms and the Macropores is greater than 1000 Angstroms (Williams & Reed, 2004).

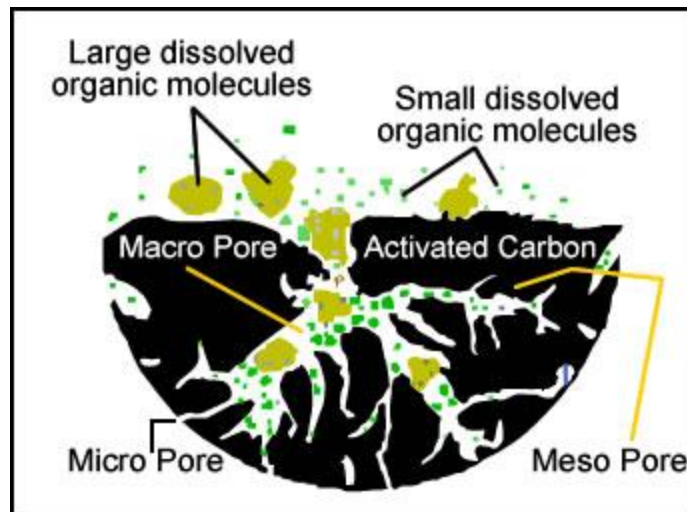


Figure 1- 5: Micropore, Mesopore and Macropore Regions of Activated Carbon

### 1.1.2 Chemical Properties of Activated Carbon

The adsorption properties of activated carbon are determined by its pore size distribution and chemical composition of the raw material. The content of natural raw materials consists of different ratio of lignin, cellulose and hemicellulose and the quality of adsorption properties strongly depends on this content (Mohamad Nor et al, 2013).

Some studies showed that the component of grape seeds or cherry stone contains a high ratio of lignin which produced improved activated carbon with a high ratio of macropores (Suhas, 2009). Other materials such as apricot stone or almond shells which have a greater content of cellulose produced activated carbon with a high ratio of micropores (Suhas, 2009).

A wide variety of functional groups presents on the surface that are usually in the form of effective edges on the microcrystalline which are heterogeneous (containing oxygen, hydrogen and nitrogen) groups in nature. These relevant functional groups containing oxygen, hydrogen and nitrogen in nature are determined by the starting materials used, oxidizing gasses which provides Oxygen and the activation method

used to produce the activated carbon. Oxygen complex group is one of the most important functional group present on the surface of activated carbon. It is formed from the reaction between carbon and oxygen that is present as a content of starting materials or from imperfect carbonization process. The oxygen content has a significant impact on the size and arrangement of initial crystallites composed in carbonaceous adsorbents. The distance between the parallel graphitic layers in adsorbents prepared from starting materials of high oxygen contents are markedly smaller (Çuhadar, 2005).

Oxidized surface carbons are generally categorized into two groups based on the acid – base attitude of the carbon. At low temperature (200 – 500°C), carbons react with oxygen to form acidic carbon. Acidic carbon is produced by chemical treatment include aqueous solution owing oxidizing agents such as chloride, permanganate, persulfate, hydrogen peroxide and nitric acid. The acid carbon surface contains functional groups such as phenolic, carboxyl, lactones and quinines groups. Acidic carbons are known as L-carbon. On the other hand, at high activation temperatures of carbon (800 – 1000°C) basic carbons are formed. Basic carbons are known as H-carbon surface oxygen complex are known as polar character of activated carbon. Acid or base surface oxide can influence the electrolyte adsorption (Çetinkaya et al, 2003).

Other heteroatoms such as (Hydrogen, Nitrogen and Sulfur) also influence the surface chemistry and form surface complexes. These complexes increase the attraction of the polar molecules on the surface complexes (Çuhadar, 2005).

## **1.2 History of Activated Carbon and Present Day Applications**

Around 1500 B.C ancient Egyptians and Phoenicians papyrus were one of the first people who used activated carbon for medical purposes and purification oils (None, 2006). Afterwards, activated carbon remained undefined as a material for adsorption until the end of eighteen century.

The earliest history when charcoal was recognized with adsorption properties was in 1773, when Swedish chemist Karl Wilhelm Scheele used carbon in experiments with gases. But modern utilization of charcoal in adsorption is connected to 1785 when lowitz paid attention to the decolorizing effects of charcoals in solutions. A few years later, charcoal was used for the purification of cane sugar. In 1793, kehli called attention to its utilized char effect, for eliminating odors from gangrenous ulcers. Throughout the nineteen century, a lot of research and studies were done to promote carbon from other source materials as decolorizing effects (Aktas et al, 2011)

Industrial production of activated carbon started when the Russian Ostrejko in 1900 patented special techniques for activated carbon production using high temperature and oxidant flows. Also activated carbon was used by the military during the First World War for making protective masks to protect against toxic gases. The uses of activated carbon have varied with the passage of time (Aktas et al, 2011).

A considerable amount of production of activated carbon is intended for the removals of pollutants from many different industrial wastewaters. The main property of activated carbon is the large porous surface areas that gives it high capability for retaining chemical materials from liquids and gases and make it versatile adsorbents. Therefore, activated carbon has been used widely in many

industrial fields. Also, activated carbon is used as a catalyst and catalysis supports for environmental issues such as separation, decomposition (Kilic et al, 2012; Mohamad Nor et al, 2013).

The utilization of activated carbon depends on its form and the media in which they are used in (liquids or gases). The main application of activated carbon in the liquid medium is related to industrials processing such as chemical process, petroleum refining, solvent recovery, metal recovery, chemical and pharmaceutical industries (Kilic et al, 2012; Okada et al, 2013). Also, activated carbon is used for water treatment and wastewater from industrial process especially to eliminate organic pollutant such as pesticides, heavy metals, odors, taste, bacteria and detergent (Durimel et al, 2013; Kilic et al, 2012; El-Deen et al; 2011). In gaseous medium, activated carbon applications are related to purification of gases such as air pollutions treatment, volatile organic compounds, separations, deodorization (Diasa et al, 2007; Mohamad Nor et al, 2013).

Generally, the powder form is used in liquid media, whereas the granular form is used in both media. The application of activated carbon usually depends on their properties (Williams & Reed, 2004).

### **1.3 Activated Carbon from Different Raw Materials**

Activated carbon is manufactured from a wide kind of carbon-rich materials. These materials include coal, wood, peat, coconut shells, bones and fruit stones. Nowadays, new materials are under investigation to be used as a source of activated carbon.

Theoretically, any organic materials with a high percentage of carbon could be activated to reinforce its sorption characteristics. Virtually, the best candidates for

activated carbon are materials which possess organic origins. Nowadays, 60% of activated carbon productions come from coal (Çetinkaya et al, 2003) .

The prevalent use of specific raw materials as a source of activated carbon is clearly bounded by the supply of those materials. Cost and the ability of activated carbon to satisfy all kinds of application. As a result, natural materials are the best candidate in the manufacture of Activated Carbon due to their good availability, being environmentally friendly, cheap and renewable materials. Lignocellulosic biomass can be considered as a massive source because it is an agriculture waste. Also, environmental problem such as water, air, accumulations pollution could be solved if the Lignocellulosic biomass by products wastes were converted to have additional worth as activated carbon, followed by coal. Also, coconut shell and peats are used to produce activated carbon but they are less available and more expensive in cost (Mohamad Nor et al, 2013).

#### **1.4 Activated Carbon Production Process**

Generally, activated carbon is manufactured by two essential activation methods, including physical (thermal) activation and chemical activation as shown in Figure (1-6) (Suhas, 2009). The characteristics of activated carbon involves; pore size distribution, shapes of the pores and surface chemistry which effectively depends on the nature of carbonaceous precursor, activation methods and activation conditions (Kong et al, 2013).

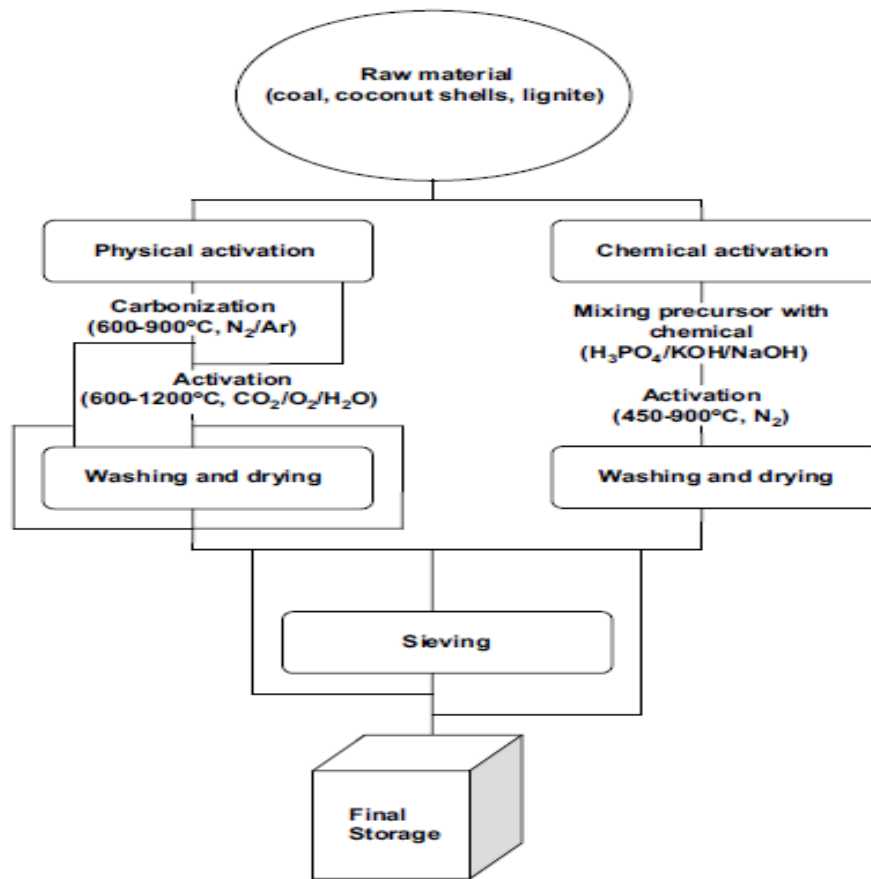


Figure 1-6: Schematic Diagram of the Production Process of Activated Carbons Adopted By Workers (Suhas, 2009).

Physical or thermal activation is one of the activation methods and consist of two steps. First step is called carbonization. Carbonization is the conversion of carbonaceous precursor to char in the absence of oxygen at high temperature (Nowicki et al, 2013), followed by the second step which is called gasification. The resulted char is exposed to high temperature in the presence of gases such as carbon dioxide (CO<sub>2</sub>) or steam (Adinaveen et al, 2013).

Chemical activation is the second activation method which is carbonization and activation of the acquired char by soaking it in chemical agents such as alkaline metal oxide or acids (Olorundare et al, 2012: Rashidi et al, 2012).

The selection of activation method plays very important roles because it determines the effectiveness of the characteristics of activated carbon such as porosity, surface area, sorption properties and activated carbon yields (Rashidi et al, 2012).

#### **1.4.1 Chemical Activation**

Chemical activation is the most popular method in recent times. Chemical activation is much easier and simpler than physical activation because both carbonization and impregnation process is carried out at the same time. Rich carbon content materials are produced as a result of the pyrolysis process with high porosity structure. Chemical agents such as  $H_3PO_4$ , HCL,  $HNO_3$ ,  $ZnCl_2$ , KOH, NaOH,  $K_2CO_3$  and  $Na_2CO_3$  can be used in chemical activation (Kilic et al., 2012; Olorundare et al., 2012). The chemical agents to activate lignocellulosic materials are usually phosphoric acid and zinc chloride which is used because it has not been formerly carbonized. Whereas, carbonized materials such as coal or chars, usually potassium hydroxide has been used as activating agent. All chemical agents used during the activation stage act as a dehydrating agent and are removed during thermal decomposition. The main aim of using chemical agent is to obtain highly developed porous structure and to reduce the creation of tar (Nabaisa et al, 2013).

The product and properties of activated carbon depend on some factors such as degree of impregnation and pyrolysis condition. Degree of impregnation also called impregnation ratio is the main important factor in the chemical activation that affects the porosity of resulting products directly. It can be defined as a ratio of the chemical agent weight to the starting materials weight. There are two mechanisms of the product based on the impregnation ratio. Micropores and Mesopores. Micropores activated carbon structures are formed when the starting material is activated with a



small ratio of chemical agents and therefore the size of pores are usually small. Whereas, by increasing the impregnation ratio of chemical agents, widening pore size activated carbon were formed which are called mesopores structure (Williams & Reed, 2004).

The properties and production of activated carbon also depend on the pyrolysis conditions such as pyrolysis temperature, soaking time and atmosphere. Pyrolysis temperature is an important factor that should be taken into account alongside the nature of the raw materials. Chemical activation is a one step process. The extent of temperature varies between (450 – 900°C) based on the nature of starting materials. Some studies showed that an increase in pyrolysis temperature led to increase mesoporous activated carbon structures product and decrease in microporous structure. Also, the Surface area of the product is affected and thus porous structures were discarded. Soaking time is a critical factor of pyrolysis condition it can be defined as the appropriate period of time to burn the sample at definite temperature. It is possible that an increase in the duration of soaking time leads to reduction of both the total pore volume and surface area due to collapse of the smaller pores (Yeganeh et al, 2006).

Chemical activation has advantages if it compared with physical activation process. These advantages include: low energy and cost process. Also, the product had better characteristics of porous structures. In addition, it has a large surface area and higher carbon yields due to prevention of formation of volatile compounds and tar because of the dehydrogenation properties of the chemical agents (Williams & Reed, 2004).. Chemical activation process requires the washing stage to remove the impurities

coming from chemical agent that may affect the properties of activated carbon. Another disadvantage is the corrosiveness of the process (Yeganeh et al, 2006).

#### **1.4.2 Physical Activation**

The main purpose of the activation process is to reinforce the pores structure. Physical activation is one of the activation methods that play a significant role in the production of activated carbon especially in the determination of the size and effectiveness of the pores. Physical activation usually consists of two steps: Carbonization and activation (Mohammad-Khah & Ansari, 2009; Mohamad Nor et al, 2013).

Carbonization is the thermal decomposition of raw materials whereby carbonaceous precursors are converted to char at high temperature (800-1000°C) in the absence of oxygen and in inert atmosphere. The main purpose of carbonization process is to reduce the non-carbon elements in the char such as oxygen, hydrogen, moisture and ash contents. During thermal decomposition of the carbonaceous precursor, oxygen and hydrogen are evaporated in the gaseous form. The product of the carbonization process contains approximately 80% of carbon contents. Residue of carbon atoms are grouped into orderly crystallographic formation known as initial graphitic crystallites followed by activation (Yeganeh et al, 2006; Adinaveen et al, 2013).

Also, activation step is related to high temperature (800 – 1100°C). It is carried out by exposing initial graphitic crystallites carbon to the action of oxidizing gasses such as carbon dioxide or steam (Kilic et al, 2012). Active oxygen in the oxidizing (activating) agent burn and react with carbon forming volatile carbon dioxide. Therefore, amount of air should be controlled throughout the activation process.

According to (Mohammad–Khah & Ansari, 2009) the mechanism of physical activation as shown below is endothermic.



During this step the pores structure have been developed and forms large pores sizes by burning the walls between pores. Whereas, the microporous structures has been reduced. The temperature degree in activation is an important measurement in the activated carbon production (Mohamad Nor et al, 2013).

For physical activation, a lot of studies showed that a steam is more effective than carbon dioxide, because it produces activated carbon with comparatively high surface area. Also, some studies show that the rate of steam activation is faster by two or three times as compared with carbon dioxide. The porosity development in the physical activation depend on (i) the activating agent. (ii) The presence of inhibition factor such as inorganic impurities. (iii) The final pyrolysis process product (Mohamad Nor et al, 2013).

## **1.5 Activated Carbon for the Adsorption of Heavy Metals**

Soil and water contamination by heavy metal is a significant concern for environmental conservation and human health (Kurniawan et al, 2011). Heavy metal compounds in wastewater and soil are produced from both industrial activities and agricultural activities such as mining, painting, metal plating, car manufacturing, and fertilizers, pulp and paper ....etc. (Fong Lo et al, 2012). All heavy metal compounds are regarded as cumulative poisons. The presence of heavy metal ions such as

cadmium, chromium, copper, lead, mercury, nickel and arsenic in soil and water are very risky to human and aquatic life because it affects the gastrointestinal track, nervous system, kidney and liver damage and others. The presence of metal ion is harmful even at micro quantities (Singh et al, 2012).

In the past few decades, removal of heavy metal ions has being the focus of many studies. Various method and techniques have been applied to remove metal ions such as chemical precipitation, membrane separation, evaporation, ion exchange, reverse osmosis and adsorption (Sekirifa et al, 2013). Most of them are considered ineffective because Heavy metal ions cannot be removed at low concentrations by classic chemical and physical treatment (Olorundare et al, 2012).

Many studies have focused on adsorbent as a low-cost, alternative and more effective than previous methods. Activated carbon gained high attention due to its low cost and adsorption capacities. Activated carbon has the ability to remove even small quantities of heavy metal ions from waste water because of the formation of complex surface between metal ions and the acidic surface functional groups of activated carbon. The effectiveness of activated carbon can be influenced by several factors including concentration of the solution, pH solution, ionic strength, formation method, chemical nature and physical properties of activated carbon (Fong Lo et al, 2012). Some metal ions have good salvation in aqueous solution. However, activated carbon can increased its adsorption rate if it is modified or made to interact with chelating agents. Simple metal ions such as mercury metal ions have being observed to be poorly adsorbed on adsorbents due to its good solvation in aqueous solution. Activated carbon is a hydrophobic adsorbent. Therefore, activated carbon cannot adsorb such ions. However, the adsorption rate of heavy metal ions can be enhanced

by pretreatment of activated carbon with some appropriate chemical agents such as precipitation, oxidation-reduction reaction and acid-base reaction or neutralization, complex formation, hydrolysis and catalytic reactions. In this way, activated carbon can combine with simple metal ions to produce precipitation, complexes or chelates and this in turn they can enhance adsorption of metal cations significantly (Mohammad–Khah & Ansari, 2009).

### **1.6 Activated Carbon for the Adsorption of Dye**

Adsorption is the most important process for non-biodegradable organic pollutants on surface and underground water sources. These organic pollutants generated from industrial activities and disposed them at the form of aqueous streams for the convergence of the outfall water on the rivers and lakes. Dyes is an important group of organic materials which have been used extensively in textile, paper and printing industries. The effluent produced from dyes industry constitute one of the problems of wastewater is not only because they contain chemical and biological compounds but also because of the colors and odors (Zümriye, 2005).

Adsorption has been proved to be the most promising option for the removal of non-biodegradable organic pollutants in aqueous solution. Activated carbon is the most prevalent for such process due to its effectiveness, versatility and low-cost. It can be used for different kind of dyes such as acidic, basic, and disperse. In addition to adsorbing organic materials, activated carbon can adsorb color, odors and other pollutants. Activated carbon can adsorb all molecules. It can adsorb even the smallest molecules if they fit the pore size (Zümriye, 2005; Suhas, 2009).

The mechanism by which adsorption of different organic compounds occur is still obscure and controversial due to its complexity. Diasa et al wrote that the subsequent argument to show with theoretical support and solid experimental: (i) aromatic compounds adsorption is partially chemical and partially physical and should accurately distinguish between them in the future work ; (ii)  $\pi$ - $\pi$  interaction might dominate under appropriate conditions and their strength can be modified by ring substitution on both, the adsorbent and the adsorbate (Kurniawan et al, 2011).

The main properties of activated carbon in the adsorption process of organic compounds are chemical contents, surface chemistry and size distribution. Capacity of adsorption is determined by accessibility of the organic molecules to the microposity which depends on the pore size because organic matter can access micropores (Kurniawan et al, 2011).

## Chapter 2

### LITERATURE SURVEY

Currently there are a lot of studies on the utilization of low-cost adsorbent from bio-sources for treatment of various polluted water. Uma et al utilized activated carbon prepared from coconut coir pith using physical activation method for the removal of MG dye in aqueous solution. The adsorbent surface area was determined to be  $205.27 \text{ m}^2 \cdot \text{g}^{-1}$ . Langmuir and Freundlich models were used to explain the adsorption isotherm and the adsorption data indicated that removal process of MG dye was better governed by pseudo-second-order kinetic than the pseudo-first-order kinetic rates at 323 k (Uma et al, 2013).

Aktas et al investigated the removal of MG dye from aqueous solution by activated carbon obtained from spent tea leaves as a waste material. Adsorption process by the spent tea leaves activated carbon (STAC) was examined by varying different variables such as ionic strength, STAC dosage, solution pH and temperature. It was determined to have considerably greater sorption capacity for MG dye. Langmuir and Freundlich model were used in the adsorption isotherm studies, and it was found the Langmuir model described the process well. The maximum adsorption capacity was found at 318 K (256.4 mg/g) while adsorption capacity increases as ionic strength decrease. The adsorption of MG dye on STAC followed the pseudo-second-order kinetic rate in kinetic studies due to their high  $R^2$  values. Thermodynamic

studies showed that the adsorption process is spontaneous and endothermic in nature of the MG dye adsorption by STAC (Aktas et al, 2011).

Hydrilla Verticillate. A submerged aquatic plant has been investigated in batch study by Rajeshkannan et al for the removal of MG dye from aqueous solution. Effects of various operating parameter, adsorbent dosage, temperature, contact time and adsorbent size were examined using response surface methodology (RSM). Optimum adsorption capacity of Hydrilla Verticillate was determined to be (91.97 mg/g) at a solution of pH 8 and it was described by monolayer Langmuir adsorption model in the adsorption isotherm. In kinetics, the results were fitted well by pseudo-second-order rate due to high value of  $R^2$ . In the sorption process, both external and intra-particle diffusion models were applied to sorption models. And it was found that both of them contribute to the actual sorption process (Rajeshkannan et al, 2010).

Alrozi et al examined Rambutan Peel-activated carbon for the removal process of the MG dye by using different reaction parameter such as initial adsorbate concentration, solution temperature, contact time and pH of the solution. In batch studies, the MG dye uptake increased with increasing initial adsorbate concentration, contact time and solution temperature. In addition, the more favorable RPAC capacity for adsorption of dye was obtained at solution pH greater than 8. Adsorption data were governed well by pseudo-second-order kinetic and Freundlich isotherm model. Moreover, the intra-particle diffusion model identified the mechanism of the sorption process. Thermodynamically, the nature of adsorption process was described to be non-spontaneous and endothermic (Alrozi et al, 2011).



Santhi et al investigated the locally available, low cost, high efficient and eco-friendly epicarp of *Ricinus Communis* based activated carbon for the removal of MG dye from aqueous solution. Various effect and adsorption parameters have been investigated such as adsorbent dosage, initial concentration, solution pH and contact time. It was concluded that the uptake percentage increased as the quantity of adsorbent increased consequently. The maximum uptake percentage of the dye occurred at pH 7 as 99.04% for CRC dose of 1 g, 50 ml<sup>-1</sup> and 25 ml<sup>-1</sup> of the initial MG dye concentration at room temperature. Moreover, the results obtained from experimental analysis indicate that adsorption behavior is described well by Langmuir isotherm. In the kinetic adsorption, it was found that the data followed pseudo-second-order kinetics rate with intra-particle diffusion model as a rate of determining step (Santhi et al, 2010).

Nethaji et al investigated activated carbon derived from *Borassus aethiopum* flowers biomass as a sorbent prepared by chemical activation for the removal of the MG dye in aqueous solution. Various parameters were studied in batch study such as adsorbent dosage, pH solution, initial dye concentration and contact time with different particle size. The zero point charge was determined as 2.5, and maximum adsorption occurred at pH range 6.0 to 8.0 at the range 78- 99 % at different concentration. Three models of isotherms were used to analyze data of experiment, and it was found that the adsorption process fitted the Langmuir isotherm model. In kinetic studies, four models such as pseudo-first-order rate, pseudo-second-order rate kinetic, Elovich model and intra-particle diffusion models were used to determine rate constant. The result obviously showed that the adsorption of MG dye onto PFAC

followed pseudo-second-order kinetic rate and intra-particle diffusion (Nethaji et al, 2010).

Also, rice straw-derived char (RSC) was studied by El-Khaiary et al for the removal of cationic dye (MG) from aqueous solution. The isotherm variables were evaluated by non-linear regression analysis. Langmuir isotherm model described well the equilibrium and maximum sorption capacity was determined at (148.74 mg/g) at 30°C. In kinetics study, it was found that the process followed the pseudo-first order model and the overall rate of dye sorption was found to be controlled by external mass transfer at the beginning of the adsorption and the intra-particle diffusion controlled the overall rate of adsorption at the later stage (El-Khaiary et al, 2008).

Also Zhang et al studied Arundo donax root derived carbon as adsorbent which was prepared by carbonization process. The effects of various parameters were studied in batch adsorption study such as solution pH, carbon dose and initial dye concentration. Optimum adsorbent dose occurred at pH solution in the range (5-7) and was determined to be 0.6 g/100ml. The data collected from equilibrium adsorption process at 293, 303 and 313 K was better described by Langmuir isotherm than Freundlich isotherm. Thermodynamically, the data evaluated from  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  showed the endothermic nature and spontaneity of the adsorption process. In addition, the result obtained in the kinetic study was well described by pseudo-second-order rate (Zhang et al, 2008).

At the end of the literature review, no one used *Ferula Communis* derived activated carbon as adsorbent for the removal of basic dye (MG) from aqueous solution.

## Chapter 3

### EXPERIMENTAL

#### 3.1 Materials and Equipments

The chemicals used are:

- Phosphoric acid (85%) from Aldrich- Germany used for chemical activation as chemical agent.
- Distilled water for washing purposes.
- Malachite Green Chloride as a dye (SIGMA-ALDRICH)
- Pieces of stem of Ferula Cummonis wood used for Charcoal production.
- Acetic acid (Aldrich)
- Sodium hydroxide (SIGMA)
- sodium bicarbonate (AnalaR)

Equipments used are listed below:

- Oven
- Mortar and pestle
- Magnetic stirrer
- mechanical shaker
- Electronic balance
- Hotplate stirrer

### **3. 2 Preparation of Activated Carbons from Ferula Communis**

The raw material chosen for the study is Ferula Communis obtained in north Cyprus from mountain areas. Pre-washed and dried pieces of Ferula Communis stem was heated at 400-500°C in the absence of oxygen and inert atmosphere in order to prepare charcoal.

The pre-heated samples were activated using chemical reagent. Briefly, 200 ml of H<sub>3</sub>PO<sub>4</sub> (85%) was added to 4.0 g of charcoal in a beaker with constant magnetic stirring and then dried in an oven at 110°C for one day. The samples was then cooled and washed with de-ionized water to remove acid residue and ash. Again, it was put in an oven at high temperature approximately (500°C) to evaporate any traces of acid remaining. Then, the sample was washed with de-ionized water again. Finally, it was cooled at room temperature and then grinded to a very tiny particle in order to produce powder activated carbon.

#### **3.2.1 FT-IR Analysis**

The FT-IR spectra of powder activated carbon were recorded on a Perkin Elmer spectrum.

#### **3.2.2 Batch Adsorption Study**

The batch studies of adsorption were carried out by mixing 0.1g of Ferula Communis Activated Carbon (FCAC) with 50 ml of different initial Malachite Green concentrations (MG) (25, 50,100mg/L) in 250 ml Erlenmeyer flask. After that, the adsorbent was separated from the aqueous phase by taking samples of adsorbate at different time intervals from 2-15 h. The dye concentration remaining in the supernatant was determined by UV/VIS spectrometer (T80 + UV/VIS spectrometer)

at 618 nm. The quantity of adsorbed dye molecules per gram of adsorbent was calculated using this equation:

$$q_e = (C_i - C_e) \frac{V}{W} \quad (1)$$

Where  $C_i$ : is the initial concentration of malachite green in (mg/L).

$C_e$ : is the equilibrium concentration of dye in (mg/L).

$V$  : is the volume of solution (L).

$w$ : is the mass of adsorbent (g).

### **3.2.3 Effect of Dosage**

Varying amounts of adsorbent (12.5, 25, 50, 75 and 100 mg) was used for the removal of malachite green. In this experiment, predetermined amounts of activated carbon was contacted with 250 ml (50mg/L) of malachite green solution at varying contact time under constant shaking at 100 rpm and at pH 6.8. After that, the samples were analyzed by UV/VIS spectrophotometer.

### **3.2.4 Effect of pH**

The effect of pH on the adsorption of malachite green by activated carbon was determined at various pH values. The pH of the solution was adjusted by addition of buffer solution at different pH (4, 6.8 and 10) at varying contact time and then analyzed using UV/VIS spectrophotometer.

Preparation of pH 4 solution:

Mix 71.1 ml of (1M) of acetic acid solution with 12.5 ml of (1M) of sodium hydroxide solution and diluted with distilled water to prepare 250 ml of solution pH4.

Preparation of pH 6.8 solution:

The preparation of solution pH 6.8 was carried out by dissolving MG dye in distilled water to prepare solution concentration (50 mg/L).

Preparation of pH 10 solution:

Mix 25 ml of (0.05M)  $\text{NaHCO}_3$  solution with 5.35 ml of (0.1M) NaOH solution and diluted with distilled water to prepare 250 ml of pH 10.

### **3.2.5 Effect of Temperature on the Adsorption Process**

The temperature effect was carried out by using (0.1 g) of activated carbon and 50 mg/L of dye solution at pH 6.8. The mixture was placed on the Hotplate stirrer in a water bath at 100 rpm at various temperatures (298, 313 and 323 K) at different time intervals (120, 300, 540, 900 and 1200 min) respectively. The dye in aqueous solutions were collected after definite intervals and analyzed spectrophotometrically.

## Chapter 4

### RESULTS AND DISCUSSION

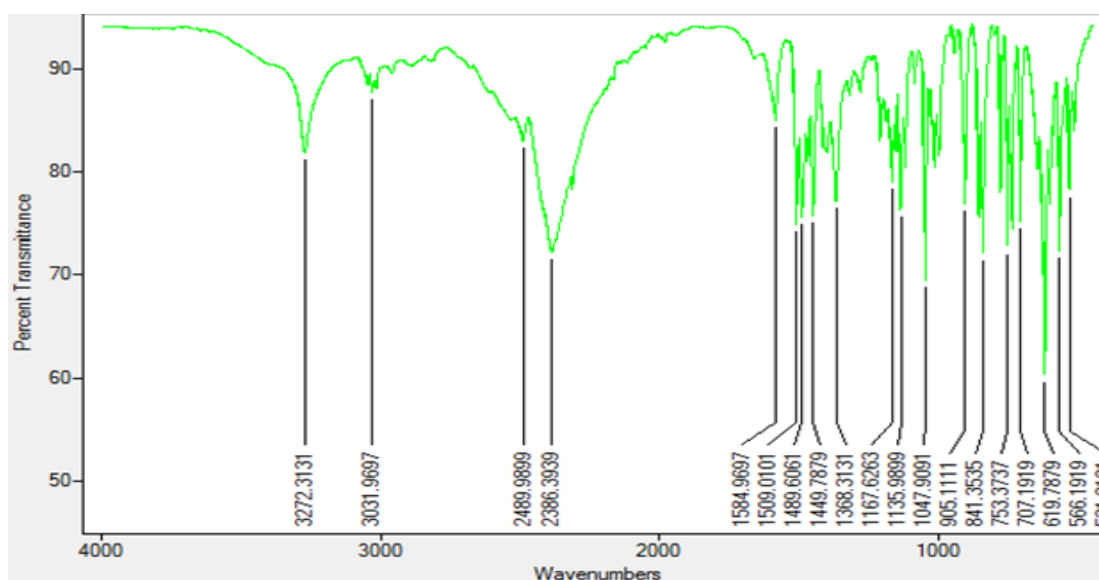
#### 4.1 FT-IR Analysis

FT-IR spectra of Malachite Green dye, Ferula Communis untreated carbon and activated carbon is shown in Figure (4-1). In the spectrum of MG dye, a lot of peaks are shown on spectrum. The most important peaks are at  $3227\text{ cm}^{-1}$  and  $3031\text{ cm}^{-1}$  are refers to the ( $-\text{OH}$ ) and C-H stretching group in methyl groups. Also, the peaks at  $1584\text{ cm}^{-1}$ ,  $1386\text{ cm}^{-1}$  and  $1167\text{ cm}^{-1}$  are referring to the C=C, C-N stretching in aromatic (Ar-CN) and C-N stretching in tertiary amine.

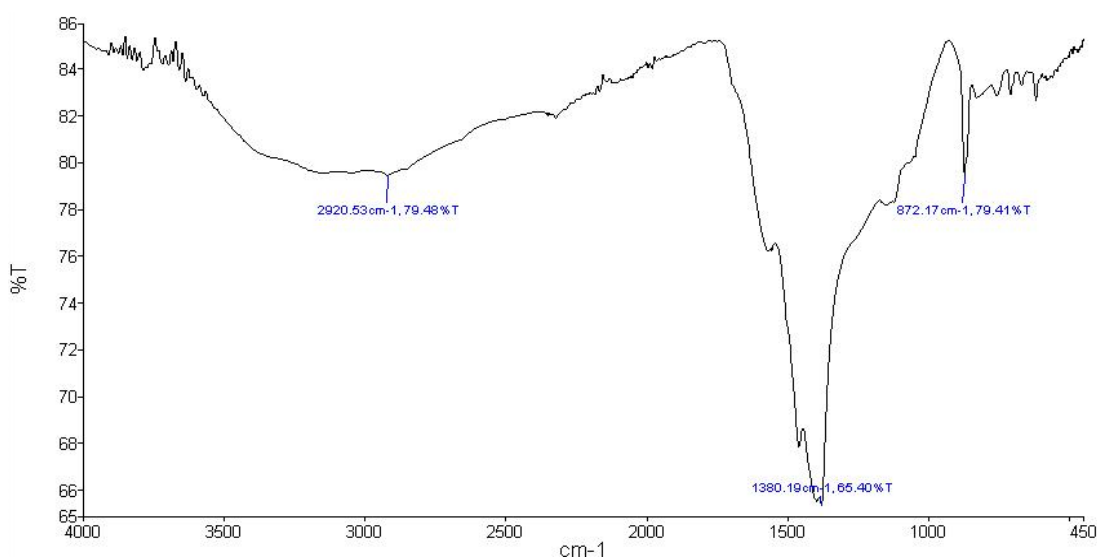
In the spectrum of raw ferula Communis charcoal. The band at  $2920\text{ cm}^{-1}$  is due to symmetric and asymmetric of C-H stretching in methyl and methylene group. The broad band  $1380\text{ cm}^{-1}$  is referring to C-N stretching group. The adsorption band at ( $618\text{ cm}^{-1}$ ) is out of plane banding stretching.

At activated carbon spectrum, there is a shifting at the band  $2943\text{ cm}^{-1}$  if it is compared with raw material which means that the of carbon occurs by phosphoric acid. Also two peaks at  $2324\text{ cm}^{-1}$  and  $1617\text{ cm}^{-1}$  are appears and refer to the R-OH group and N=O group respectively. The peak at  $1127\text{ cm}^{-1}$  is refer to the lignin structure.

As a regard to the FT-IR spectrum of the dye loaded activated carbon and its comparison with activated carbon, there is a decrease in peak at  $1617\text{ cm}^{-1}$  in FCAC to  $1579\text{ cm}^{-1}$  in FCAC-dye. Also, this peak becomes stronger and broader in FCAC-dye. These decreases can be ascribed to the interactive adsorption of MG dye onto surface of FCAC. In addition, the spectrum of FCAC- dye show an increasing in the peak at  $1167\text{ cm}^{-1}$  if it is compared with the FCAC spectrum due to the bonding between FCAC structure and MG dye.

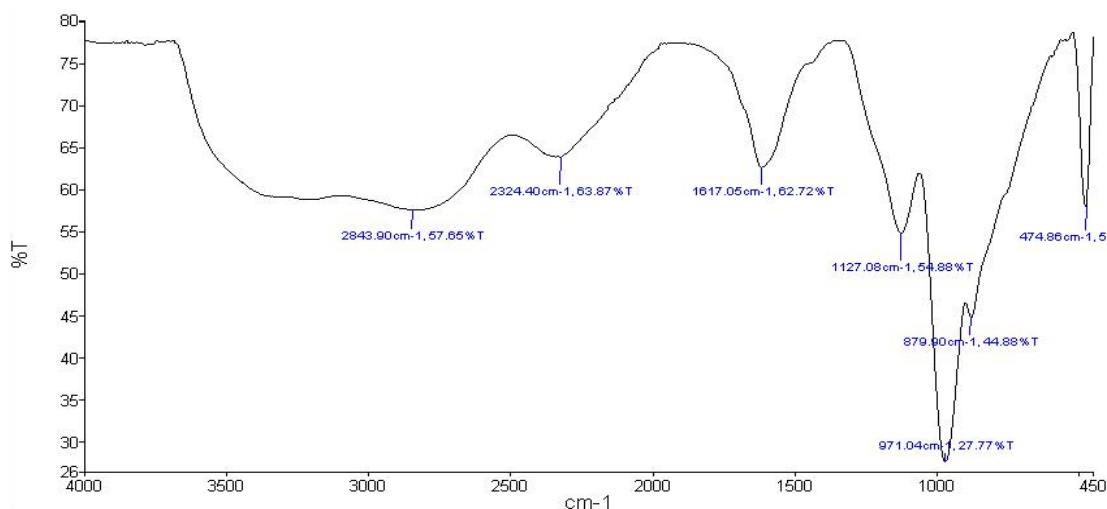


a) MG dye spectrum

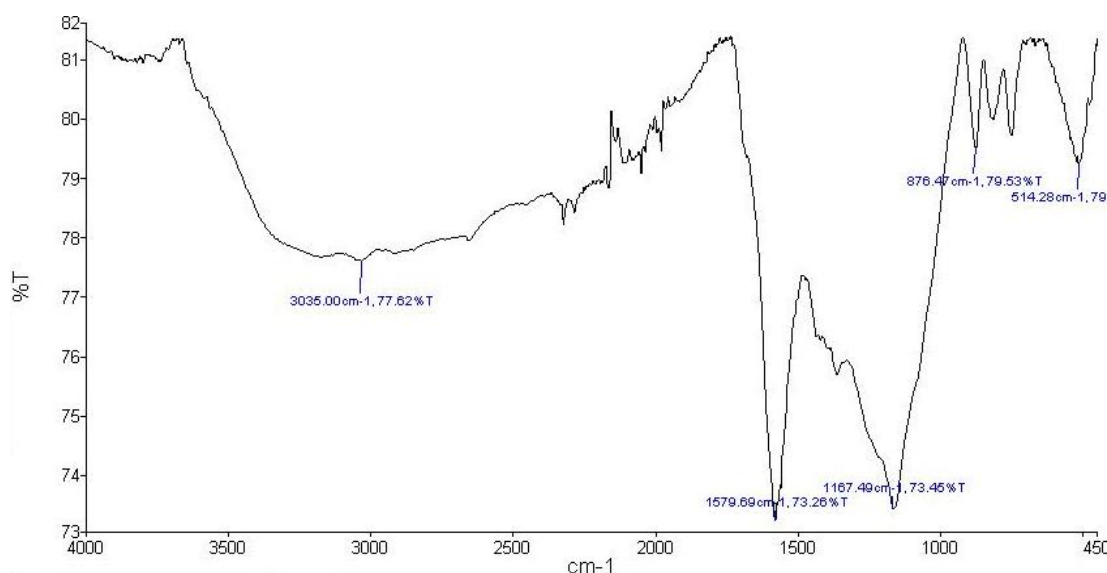


b) Raw material





c) Ferula Communis Activated Carbon (FCAC)



d) FCAC- dye loaded

Figure 4-1: FTIR Analysis of a) Malachite Green, b) Raw Ferrula Communis, c) Activated Carbon Prepared By Chemical Activation And d) Dye Loaded Activated Carbon

## 4.2 Adsorption Calibration Curve

Different concentrations of the MG dye solution (100ml, 50ml, 25ml and 12.5ml) were prepared from stock solution (200mg/L) by serial dilution. The adsorbances of each MG dye solution were measured individually by Perkin-Elmer UV/VIS spectrophotometer. From the results obtained, a plot of concentrations (mg/L) on the

x-axis versus absorbance (Abs) on the y-axis was plotted and the graph of the calibration curve drawn as shown in Figure (4-2). The amount of equilibrium concentration was obtained from the calibration curve by the following equation:

$$y = ax + b \quad (1)$$

Where  $y$  - Absorbance.

$a$  - Intercept.

$b$  - Slope.

$x$  - Equilibrium concentration

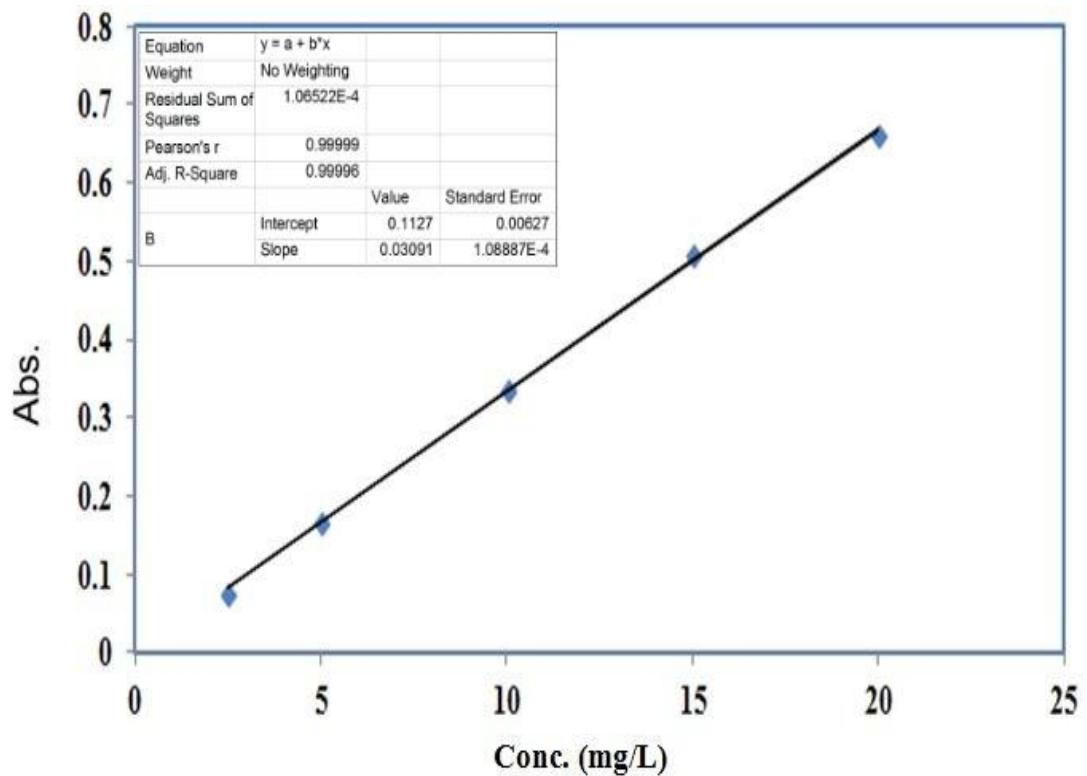


Figure 4-2: Calibration Curve of Malachite Green Dye at Different Concentration..

### 4.3 Batch Study of Dye Adsorption

The batch study of MG dye was achieved after preparing different solution concentrations and placed on the shaker for 15 h as mentioned in the section (3.2.3).

The adsorption capacity and removal percentage of the adsorbent after UV/VIS spectrophotometer reading was obtained and analyzed by using both equations below. In addition, all MG dye solution concentrations was determined at the wave length 618 nm corresponding to the highest absorbance of each dye solution.

$$q_e = (C_i - C_e) \frac{V}{W} \quad (2)$$

Where  $q_e$ : is represented the equilibrium concentration of sorbed MG in solid sorbent.

$c_i$ : is the initial concentration of MG dye and

$c_e$ : is the equilibrium concentration of MG dye (mg/L).

$w$ : is the weight of FCAC (g).

$v$ : is the volume of MG dye solution in (L). The removal percentage of MG dye also calculated using equation bellow.

$$\text{Removal \%} = \left( \frac{C_i - C_e}{C_i} \right) 100 \quad (3)$$

#### **4.3.1 Effect of Adsorbent Dose on Adsorption Process**

To optimize the adsorbent dose for the removal of MG from its aqueous solutions, adsorption was carried out with different adsorbent dosages at room temperatures. The amount of the dye removed by adsorption on FCAC is presented in Figure (4-3). The dose of adsorbent was varied from 12.5mg to 100mg for FCAC at fixed pH of 6.8. The study shows an increase in adsorption with the increase in dosage of the adsorbent. As the adsorbent dosage increases, the surface area and adsorbent sites available for the dye molecules also increase and consequently better adsorption

takes place. In the case of FCAC at room temperature, the uptake of dye increases from 110mg/g at 12.5mg to 230mg/g at 100mg.

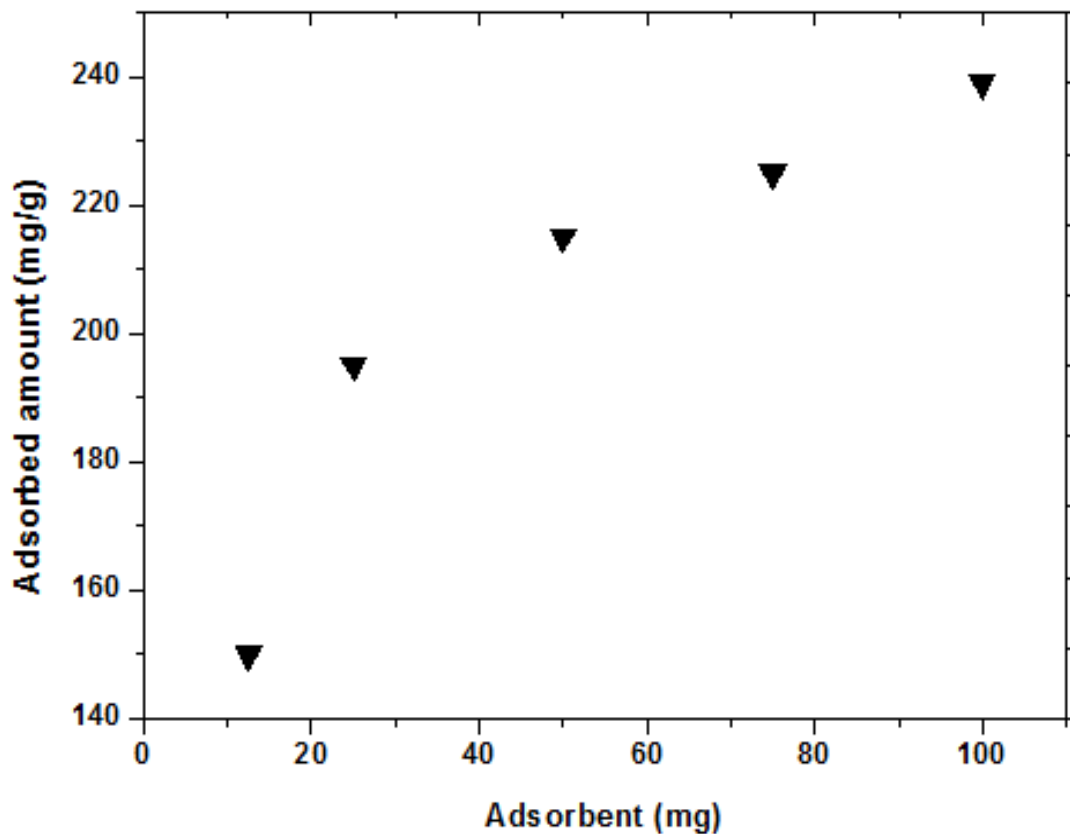


Figure 4-3: Effect of FCAC adsorbent dosage ([MG dye]= 50 mg/L; t=900min; shaker =100rpm ; pH=6.8; T=298K).

#### 4.3.2. Effect of Initial Adsorbate Concentration on Adsorption Process

Initial concentrations of MG dyes was changed in order to determine maximum MG dye adsorption keeping the contact time 900 min for FCAC at a fixed dose 100mg for FCAC at pH (6.8). Figure (4-2) showed that the amount adsorbed  $q_e$  increased with an increase in the dye concentration. these increases was prospective due to the driving forces produced from a higher concentration gradient between adsorbate in solution and adsorbate on the FCAC surface at higher initial dye concentration.

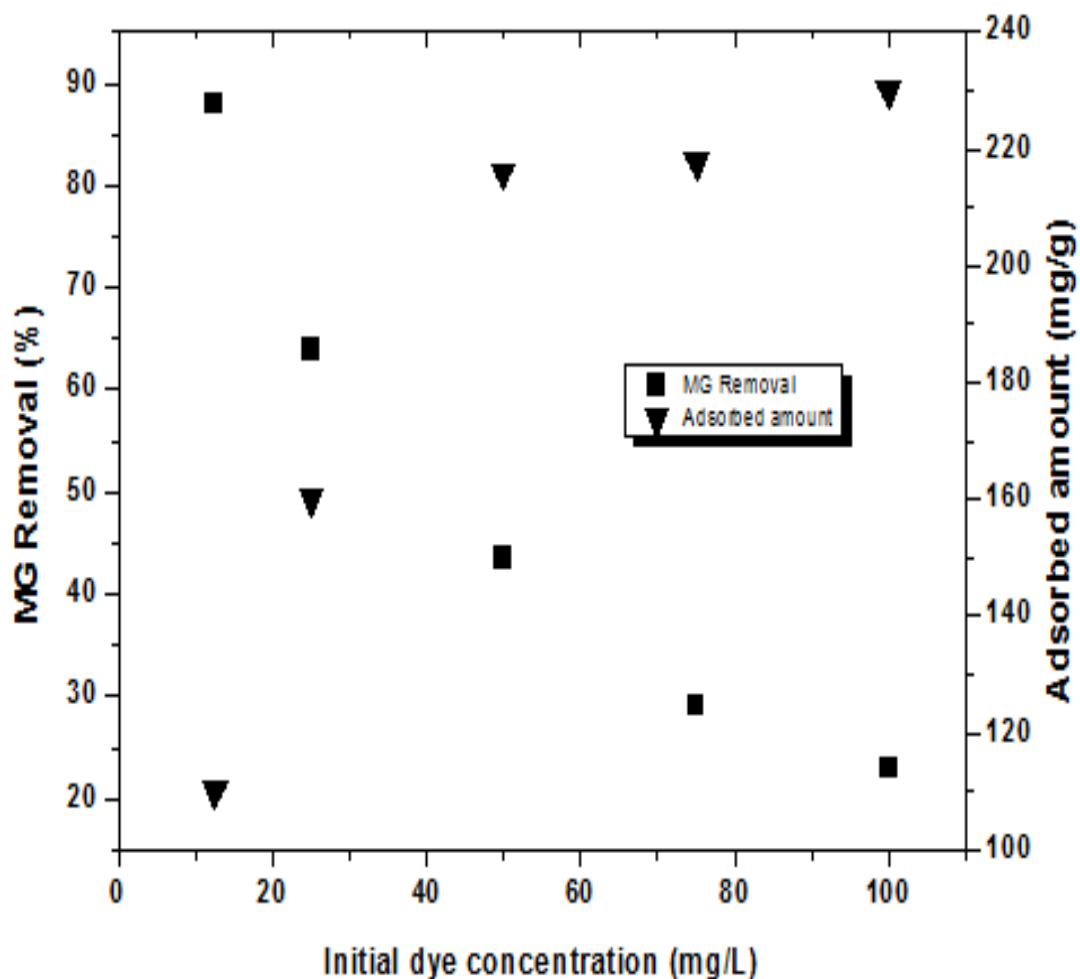


Figure 4-4: Effect of initiation dye concentration ([FCAC adsorbent]= 100mg; t=900min; shaker=100rpm ; pH=6.8).

Moreover, percentage removal rate decreased with an increase in the dye concentration. It was also noted that the rate of removal of the dye is faster at lower concentration and decreases with increasing concentration. It is apparent from the figure that with increasing concentration of the dye from 12.5 mg/L to 100mg/L, the percentage removal decreases from 88 to 5.75% for FCAC. Adsorption of the dye was found to increase linearly with increasing concentration of adsorbate for FCAC in the concentration range from 12.5 mg/L to 100mg/L. this phenomenon can be explained that all adsorbate ions could interact with the binding active site on the surface of adsorbent in the sorption medium at low concentrations and hence higher removal percentage result. While, at higher concentrations, the adsorption active sites

on the surface of FCAC has been saturated and therefore, the removal percentage of the dye by FCAC shows a decreasing trend.

#### 4.3.3 Effect of pH on the adsorption of MG dye onto FCAC

Effect of PH solution is one of the most important parameter on the adsorption capacity because it is affect both degree of ionization of dye and surface properties of the biosorbent. Effect of solution pH on the adsorption as shown in figure (4-5) was studied by varying pH of the dye solution (4, 6.8 and 10).

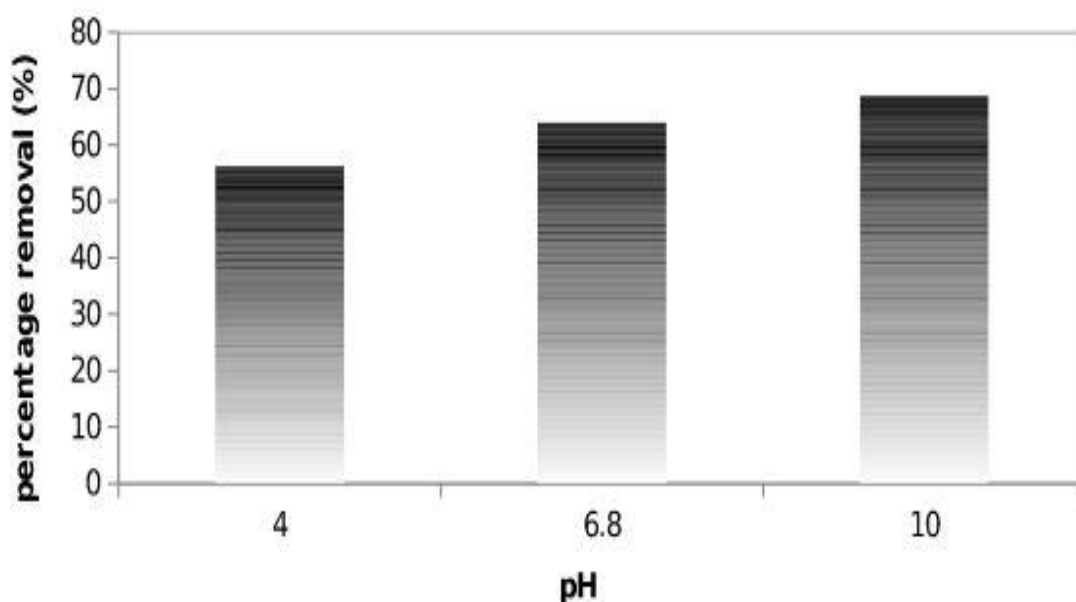


Figure 4-5: Effect of pH ([MG dye]= 50mg/L; [FCAC adsorbent]= 100mg; t=900min; shaker=100rpm).

While, other parameter such as initial dye concentration, adsorbent dosage, contact time and agitation speed were fixed at 50 mg/L, 100 mg, 900 min and 100 rpm respectively.

Basically, the maximum removal percentage obtained at pH solution 10 and the minimum percentage removal occurs at pH solution 4. This minimum at acidic solution may due to the hydrophobicity of AC which caused to absorb hydrogen ion

onto the surface of the carbon when submerged in water and made it positively charged.

#### **4.3.4 Effect of Temperature On The FCAC Adsorption**

Adsorption of MG dye on FCAC at different temperatures was investigated as a function of contact time (120, 300, 540, 900 and 1200 min) in order to determine the removal percentage of MG dye. This study was investigated at 298, 313 and 323 K as shown in Figure (4-6) below. While other parameter such as adsorbent dosage, initial dye concentration and shaker was at 100mg, 50mg/L and 100 rpm respectively. It was observed from Figure (4-6) that as the time increases, the adsorption process increased but with decrease in temperature. This phenomenon indicated that the equilibrium uptake decreased as the temperature increased. It shows that the dye adsorption reaction nature is exothermic. In addition, the amount of MG dye adsorbed on the active sites increased during early stages which led to decrease in the mobility of the diffusion molecules of MG dye to pass through the solution in long period for adsorption.

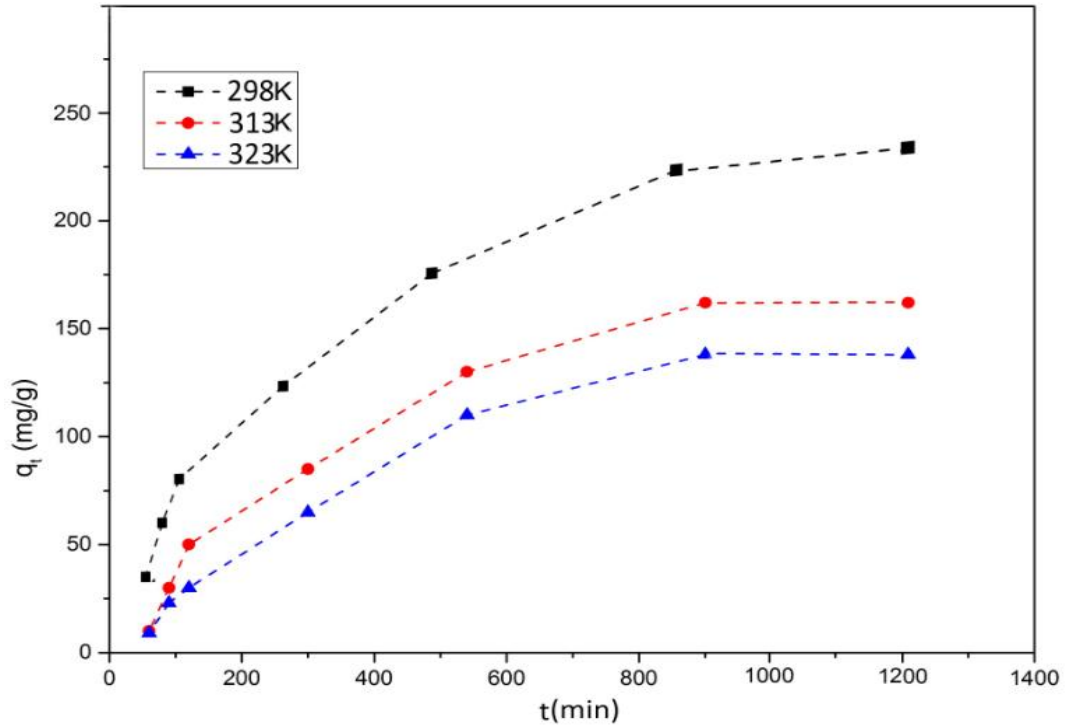


Figure 4-6: Effect of Temperature ([MG dye]= 50 mg/L; t=1200min; shaker=100rpm).

#### 4.4 Adsorption Isotherm Study

Langmuir and Freundlich isotherm models were used to describe the equilibrium characteristics of adsorption. Adsorption isotherm is proved when the quantity of solute being adsorbed on the adsorbent is equal to the quantity being desorbed. Langmuir model is effective for monolayer adsorption on specific homogeneous adsorbent surface sites. The surface are of Adsorbent composed of identical active sites with equal energies and equal available for adsorption.

Table 4-1: Estimated equilibrium parameters of Freundlich and Langmuir isotherms for MG

Equilibrium isotherm							
Temperature (K)	$q_{exp}$ (mg/g)	Langmuir model			Freundlich model		
		$q_m$ (mg/g)	$b_m$ (L/g)	$R^2$	$K_f$ (mg/g)	$n$	$R^2$
298	243.6	239.9	23.99	0.9987	107.8	3.057	0.8795
313	168.5	169.1	23.38	0.9998	167.3	3.732	0.9145
323	123.8	121.5	22.69	0.9997	175.9	5.094	0.8999



Langmuir model assumes that adsorption occurs at specific homogeneous sites with the adsorbent and each dye molecule occupying one site only. Non-linear and linear Langmuir isotherms are represented by following equations:

$$q_e = \frac{q_m b_m C_e}{1 + b_m C_e} \quad (4)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m b_m} + \frac{C_e}{q_m} \quad (5)$$

Where  $c_e$  is the equilibrium concentration of the adsorbate ions (mg/L),  $q_e$  is the quantity adsorbed (mg/g) the constants  $q_m$  is the monolayer adsorption capacity (mg/g) and  $b_m$  are related with the adsorption energy (L/mg). The values of  $q_m$  and  $b_m$  can be calculated from the linear plot of  $c_e/q_e$  versus  $c_e$ . Freundlich isotherm model assumes a heterogeneous surface with a non-uniform distribution of heat for adsorption over the surface. Non-linear and linear Freundlich equations can be expressed by the following equation:

$$q_e = K_f C_e^{1/n} \quad (6)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln c_e \quad (7)$$

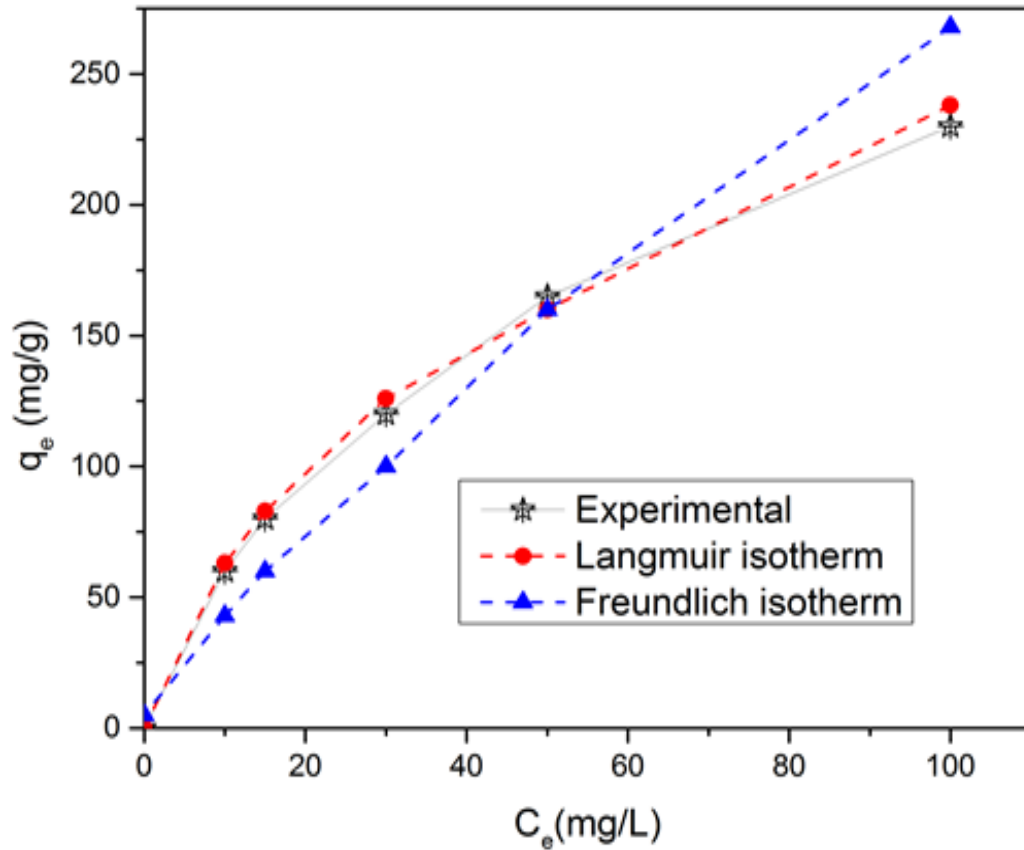


Figure 4-7: Nonlinear Equilibrium Plot for Dye Removal ([MG dye] = 50 mg/L; t=900min; shaker=100rpm).

Where  $q_e$  represent the quantity adsorbed (mg/g),  $K_f$  is the adsorption capacity (mg/g),  $c_e$  is the equilibrium concentration (mg/L) and  $1/n$  is a measurement of adsorption intensity.

After fitting the results obtained from experiments in the Langmuir and Freundlich isotherm equations (5 and 7) the result and values of the evaluated parameters are calculated and shown in Table (4-1). Figure (4-8) describes the fitted equilibrium data in the Langmuir and Freundlich isotherm.

From the isotherm parameters obtained as indicated in Table (4-1) and plotted in Figure (4-8). it can concluded that the Langmuir isotherm fits the data better than

Freundlich isotherm. Also this is supported by the high values of the correlation coefficient  $R^2$  in case of Langmuir isotherm (more than 0.99) as compared with Freundlich isotherm (0.90). The best fit of equilibrium isotherm data in the Langmuir isotherm expression confirms the monolayer adsorption of the MG cationic dye onto FCAC.

In addition, FCAC sorbent investigated in this work has comparatively high adsorption capacity (239.9 mg/g) for the removal of MG dye from aqueous solution as shown in Table (4-1). To compare the adsorption capacity of FCAC with various adsorbents used for the adsorption of MG dye is shown in Table (4-2) below.

Table 4-2: Comparison of adsorption capacities of various adsorbent on of MG dye

Adsorbents	Adsorbate (dye)	$q_m$ (mg/g)	Reference
Rambutan peel AC	MG	329.41	Alrozi et al, 2011
Spent Tea leaves AC	MG	256.4	Aktas et al, 2011
Ferula Cummonis AC	MG	239.9	this work
Rice Strew- derived char	MG	148.74	El-Khaiary et al, 2008
Hydrilla Verticillate AC	MG	91.97	Rajeshkannan et al, 2010
Burassus Aethiopum flower AC	MG	48.48	Nethaji et al, 2010
Cocount Coir pith AC	MG	27.44	Uma et al, 2013
Arunda-Donax root	MG	8.69	Zhang et al, 2008

Moreover, in order to ensure that the adsorption process is favorable, irreversible or unfavorable for Langmuir kind adsorption process. Langmuir isotherm is then categorized using a dimensionless constant separation factor ( $R_L$ ), which can be defined as:

$$R_L = \frac{1}{1+b_m C_i} \quad (8)$$

Where  $c_i$  (mg/L) is referring to the highest initial dye concentration and  $b_m$  (L/g) is referring to the Langmuir constant. The parameter  $R_L$  value reveals whether adsorption system is irreversible ( $R_L = 0$ ), unfavorable ( $R_L > 1$ ) or favorable ( $0 < R_L < 1$ ) in batch study. The  $R_L$  values obtained from the above equation for the sorption of MG dye on the FCAC are (0.00166, 0.0008 and 0.00041) at various temperature (298, 313 and 323 K) respectively. The results calculated falls in the range between 0 and 1. It can therefore be concluded that the sorption is favorable and supports the Langmuir isotherm.

#### 4.5 Adsorption Kinetic Modeling

In kinetics studies, Lagergren pseudo-first-order kinetic model and pseudo-second-order kinetic model by HO and McKay were applied to the adsorption experimental data in order to analyze the adsorption kinetics of MG dye on FCAC. To predict sorption kinetic, pseudo-first-order kinetic model was defined as follow

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (9)$$

Where  $q_e$  and  $q_t$  are the amount of MG dye (mg/g) adsorbed at equilibrium at any time (t) respectively.  $k_1$  (1/min) is the rate constant for the sorption. The straight line plots of  $\ln(q_e - q_t)$  versus time (t) at various temperatures (298, 313 and 323 K) is illustrated in Figure (4-8).

From Table (4-3), the values of the correlation coefficient ( $R^2$ ) are low and the values of  $q_e$  calculated from linear plots do not confirm the values of  $q_e$  in experimental. This confirms that the adsorption of MG dye onto FCAC does not follow pseudo-first-order kinetics.

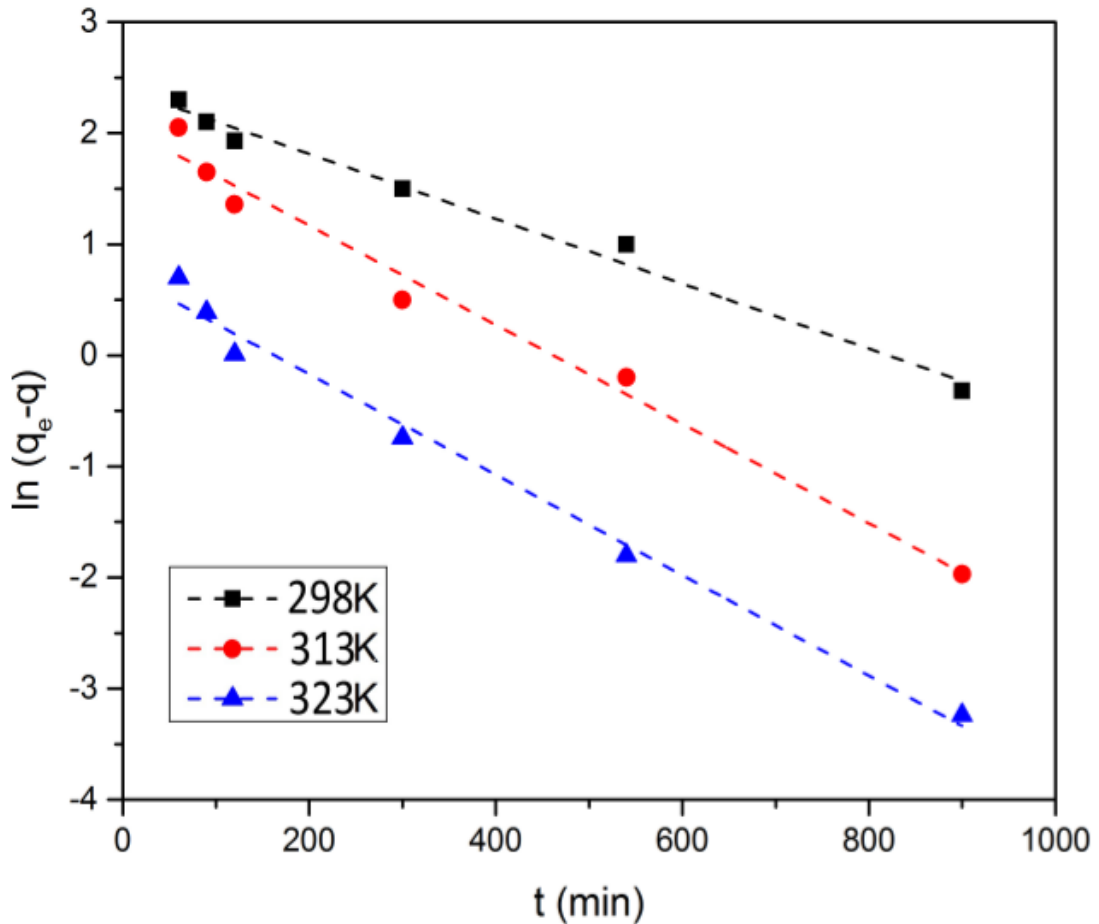


Figure 4-8: Pseudo-First-Order Kinetic ([MG dye]= 50 mg/L; t= 900min; shaker=100 rpm ; pH=6.8).

For pseudo-second-order kinetics model, it can be described as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Where  $k_2$  is the rate constant of pseudo-second-order ( $\text{gm.mg}^{-1}.\text{min}^{-1}$ ). The value of

$1/q_t$  and  $1/k_2q_e^2$  can be estimated from the slope and intercept respectively of the straight line plots of  $1/q_t$  versus  $t$  as shown in Figure (4-9).

Table 4-3: Kinetic parameters for MG adsorption onto MFC-AC

Kinetic models							
Temperature (K)	$q_{exp}$ (mg/g)	Pseudo-first order model			Pseudo-second order model		
		$q_e$ (mg/g)	$k_1$ (1/min)	$R_2$	$q_e$ (mg/g)	$k_2$ (g/mg min)	$R_2$
298	197.5	109.9	0.0171	0.8887	207.9	0.035511	0.9995
313	161.5	89.1	0.0123	0.7898	167.3	0.009621	0.9985
323	120.8	161.5	0.0151	0.8397	135.9	0.001758	0.9999

The value of  $q_e$  obtained from pseudo-second-order model along with correlation coefficient as shown in Table (4-3) indicated that the  $q_e$  values are very close to  $q_e$  in experimental values and the values of the correlation coefficient are also greater than (0.99). The study proposes that the adsorption process of MG dye onto FCAC follows pseudo-second-order kinetic model.

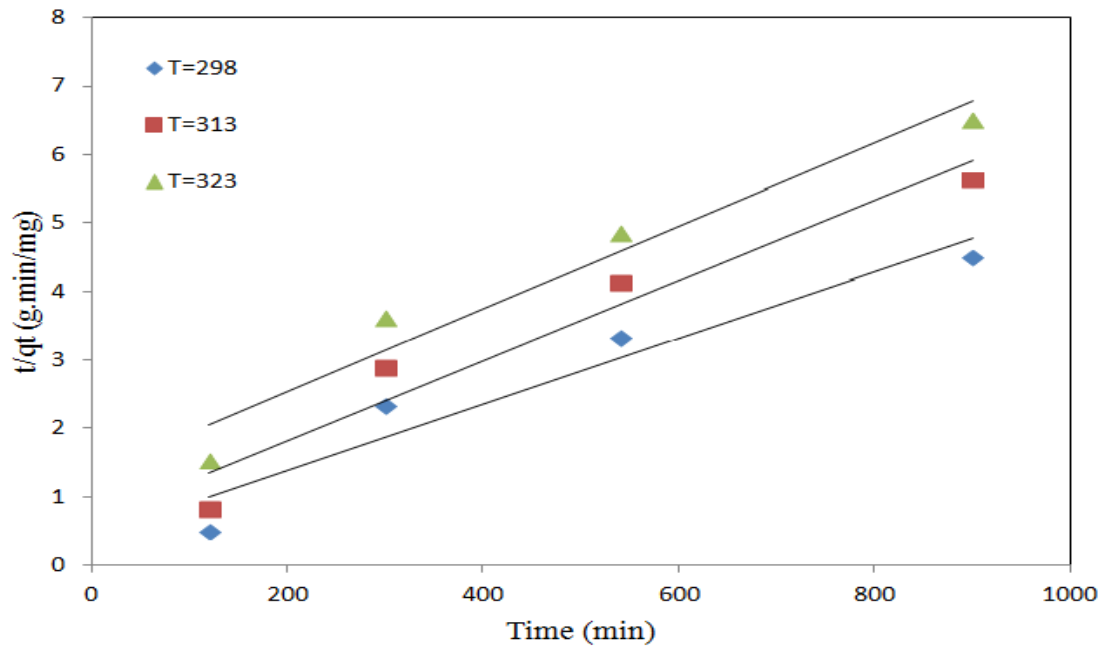


Figure 4-9: Pseudo-Second-Order Kinetic ([MG dye]= 50 mg/L; t=900min; shaker=100rpm ; pH=6.8).

## Chapter 5

### CONCLUSION

First of all, activated charcoal can be obtained from *Ferula Communis* charcoal under proper modification by chemical activation with phosphoric acid ( $H_3PO_4$ ) is effective for the removal of Malachite Green dye (MG) from aqueous solutions. The maximum adsorption capacity was obtained at 298 K temperature ( $239.9 \text{ mg.g}^{-1}$ ).

- FT-IR analyses provide evidence for the functional groups on the sorbent surface which was ascribed to be liable for MG dye adsorption.
- The adsorption data obtained followed the Langmuir isotherm which was best illustrated by the correlation factor ( $R^2$ ) and the maximum adsorption capacity for MG dye on FCAC.
- The kinetic studies showed that all the adsorption data of adsorption process was well described by the pseudo-second-order kinetic rate at the various temperatures investigated as depicted by the ( $R^2$ ) value.
- The adsorption process was found to be exothermic due to increase in adsorbed capacity as temperature decreases.

*Ferula Communis* that was used in this investigation is a natural, renewable, abundant and local plant widely available in Cyprus and the Mediterranean basin countries. *Ferula Communis* based activated carbon can be used for wastewater treatment for MG and other related basic dyes of this dye class.



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