

**An-Najah National University**  
**Faculty of Graduate Studies**

**Treatment of Organic Phenolic Contaminant In  
wastewater Using Activated Carbon From Cypress  
Products**

**By**

**Nadeem Hamdallah Jameel Bassalat**

**Supervisor**

**Dr. Shehdeh Jodeh**

**Dr. Ahmad Abu Obed**

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the Degree of Master in Environmental Science, Faculty of Graduate  
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**This thesis was defended successfully on 26 /12 /2012 and approved by:**

**Defense Committee Members**

**Dr. Shehdeh Jodeh / Supervisor**

**Dr. Ahmad Abu Obed / Co-Supervisor**

**Prof. Ibrahim Kayaleh / External Examiner**

**Prof. Marwan Haddad/ Internal Examiner**

**Signature**

  
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### III

#### **Dedication**

This work is dedicated to my beloved mother, Rana, Ahmad, Batool, Sara and Hamdallah for their endless support, love, encouragement and understanding.

To my brothers and sister for tremendous help.

I don't forget to dedicate this work to my solemn father (mercy to him) who had sacrificed intently for the sake of our education before he passed away.

## **Acknowledgement**

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Many thanks for my friends in Hajja school for encouragement.

And at last my great thanks, gratitude love to my mother.

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

## **Treatment of Organic Phenolic Contaminant In wastewater Using Activated Carbon From Cypress Products**

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه  
حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم لنيل أية درجة أو لقب علمي أو بحثي  
لدى أية مؤسسة تعليمية أو بحثية أخرى.

### **Declaration**

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student Name:

اسم الطالب:

Signature:

التوقيع:

Date:

التاريخ:

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### List of Abbreviation

Symbol	Abbreviation
A	Intra-particle diffusion constant gives an idea about the thickness of the boundary layer.
Abs.	Absorbance
AC	Activated carbon
B	Langmuir constant related to the rate of adsorption
Ce	Concentration of PNP at equilibrium.
C0	Initial liquid-phase concentration of adsorbate.
CFAC	Cypress fruit activated carbon
EPA	Environmental Protection Agency
IN	iodine number (mg/g),
k1	Equilibrium rate constant of pseudo-first-order kinetic model.
k2	Equilibrium rate constant of pseudo-second-order kinetic model.
K*2	Equilibrium rate constant of second-order kinetic model.
K <sub>F</sub>	Freundlich constant represents the quantity of adsorbate onto activated carbon per a unit equilibrium concentration
N	Freundlich constant
N	normality of sodium thiosulfate solution
PNP	Para-nitrophenol
PR	percentage removal (%)
qe	Amount of adsorbate per unit mass of adsorbent at equilibrium(min).
qt	Amount of adsorbate per unit mass of adsorbent at time t (min).
R <sup>2</sup>	Correlation coefficient
R <sub>L</sub>	separation factor
Vb	are volumes of sodium thiosulfate solution required for blank
V <sub>C</sub>	cylinder volume packed with dried activated carbon (ml)
V <sub>s</sub>	Vs are volumes of sodium thiosulfate solution required for sample titrations (ml)
Wa	weight of crushed cypress fruit sample after carbonization
Wb	weight of crushed cypress fruit sample before carbonization
Wb1	weight of beaker containing dried sample (g)
Wb2	weight of beaker containing original sample of CFAC (g)
Wc	weight of original sample used of CFAC (g).
W <sub>C1</sub>	weight of cylinder and CFAC (g)
We	weight of empty cylinder
W <sub>S1</sub>	weight of original CFAC used (g).
W <sub>S2</sub>	weight of crucible (g),
W <sub>S3</sub>	weight of crucible containing ash (g),

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**Abstract**

This thesis work focuses on preparing and studying the properties of activated carbon produced from cypress fruit by chemical activation using phosphoric acid ( $H_3PO_4$ ) as an activating agent, and then studies the mechanism and effectiveness of this carbon to adsorb p-nitrophenol (PNP) from the aqueous solution because the phenolic organic compounds are extremely highly generated from many resources which disposed to sewerage system or valleys without treatments that increase the risk of contaminating water resources.

Tubular regulated furnace was used for cypress fruits carbonization at  $700^{\circ}C$ , then characteristics of prepared activated carbon were studied. Surface area was determined using iodine number and standard calibration curve for iodine number. PNP adsorption onto activated carbon surfaces was studied by batch experiments. The adsorptive properties of cypress fruit activated carbon (CFAC) were investigated in terms of adsorbent dose, PNP concentration, pH, temperature and contact time in a batch system. To investigate the nature of the surface and adsorption capacity of CFAC, Freundlich and Langmuir models were used to study adsorption process at equilibrium. In order to determine whether the adsorption process is chemical or physical, four kinetics models were used to describe

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the adsorption process, pseudo-first order kinetic models, pseudo-second order kinetic models, second order kinetic models and Intra-particle diffusion model.

Results show that the activated carbon produced from cypress fruit gives good percentage yields which reach up to 51.8%. Surface area determined by iodine number showed 524.1 m<sup>2</sup>/g.

Results indicate that the optimum percent of PNP removal was 90.9 % when adsorbent dosage was 0.3g and PNP concentration 80mg/L. Percentage removal of PNP increases when the concentration of PNP decreases as the maximum percentage removal reached 93.2% when PNP concentration was 20mg/L and 0.1g CFAC. At lowering pH from 6 to 2 it was found that PNP adsorbent increases slightly , but the decrease of adsorbent at pH from 6 to 12 is highly extreme. The effect of temperature on adsorption by CFAC has also been investigated in the range of 15-45 °C. The results indicate that the temperature slightly affected the effectiveness of CFAC adsorption. The results showed that the equilibrium time for PNP adsorption is 150min, but most of the adsorption attained within the first ten minute.

Results investigate that the produced CFAC adsorption equilibrium is represented by both Frenundlich and Langmuir equilibrium model, but Langmuir model describe very well the adsorption. The main properties of Langmuir equation can be expressed in term of separation factor,  $R_L$ . The  $R_L$  equal 0.053 that indicate the adsorption is favorable.

The rate constants for the kinetic models were determined and the correlation coefficients were calculated. The kinetic data for adsorbents supports pseudo-second order model for PNP adsorption with correlation coefficient values ( $R^2$ ) and  $k_2q_e$  of 0.9994, 0.502, respectively.

The values of the intra-particle diffusion constants and the correlation coefficients imply that the rate of PNP adsorption onto CFAC is limited by mass transfer across the boundary layer.

## **Chapter One**

### **General Introduction**

#### **1.1 Overview**

Pollution is considered to be one of the most difficult problem that influence all our life aspects and environment, and it's become clear to everyone.

Because of this, contaminant of environment become one of the most serious issues that all the countries around the world are concerned about.

Year by year, the pollution problem enlarged by the population growth increase. This increase in demand for natural resources especially water and food supplies that increased stress on the ground and surface water quality and quantity.

One of the environmental problems that has become an increasingly important issue in developed and developing countries is pollution of surface and ground water with phenolic compounds.

Industry revolution process especially in agroindustry, petrochemical industry, and oil industry generate phenol and phenolic derivative which appear in wastewater that is usually more than the threshold level which is considered as a safe level. Management of this wastewater becomes the main challenge in management of wastewater.

Scarcity and limited access to water resources in Palestine have been a major issue, which requires preservation of existed resources from possible contamination with pollutants. Different types of point and non-point pollution sources contribute to this problem, including industrial and agricultural activities. One of the major pollution sources is semi-solid effluent (Alzibar), generated seasonally from olive oil extraction processes. Its discharged to valleys without pre-treatment, and may contaminate groundwater resources, mainly due to its high phenolic content. The current



and future wastewater treatment plants in West Bank are designed on a basis that does not take into account sudden overloading, and shocks related to semi-solid effluent (Alzibar) discharges, which may threat their functionality. Contamination from semi-solid effluent (Alzibar) is a major problem in developing countries, where sophisticated treatment technologies are too expensive. Therefore, effective and feasible pre-treatment of olive mill wastewater must be considered. Several methods used to remove phenol and other phenolic compounds from waste water. Biochemical oxidation is the base of many methods but these methods suffer from limitation as; low efficiency in the removal of low concentration. Activated carbon (AC) is the carbonaceous material which plays an important role in adsorption process and it's using is consider to be an effective method in removing organic and inorganic chemical waste, odor and color from any kind of chemical industry process. This tremendous use because it has amazing properties. AC has large surface area for interaction with polar or non polar adsorbates, micro-porous properties, capacity of adsorption, high purity and easy to be available [1]. Many studies investigate the adsorption of phenol and other phenolic compounds on AC prepared from agricultural by-products, and low-rank coals [2].

The AC can be derived from many agricultural raw materials for example rice husk, olive waste, date stone and other agricultural residuals. Using agricultural by-products and unused agricultural products have many advantage as; change unwanted agricultural product or agriculture waste to more useful products, increasing used of AC to remove contaminants of environment. Producing AC based on two main steps. First, carbonization

under nitrogen gas flow with high temperature. Second, activation which may be achieved chemically using chemical agent or physically [3].

## **1.2 Objectives of this Work**

### **1.2.1 General objectives**

In Palestine, phenolic compounds contamination due to olive mill wastes which contaminate the soil in agricultural fields, surface and ground water is becoming a major contributors of pollution in Palestine and Mediterranean region. Therefore, the overall goal of this research was to find practical and economical way to reduce phenolic compounds concentrations in ground and surface water that can be used in Palestine and other Mediterranean countries by producing activated carbon from cypress fruit product and investigate the feasibility to adsorb phenolic compounds which may be used to reduce the environmental impact of these compounds.

### **1.2.2 Technical objectives**

The objective of this project is focused on preparing low cost carbon adsorbent from cypress fruit and using it for water purification from phenolic compounds. While achieving this objective, the following technical objectives will be achieved:

1. Prepare activated carbon from cypress fruit using phosphoric acid as activation agent.
2. Determine activated carbon characterizing.
3. To study surface area of activated carbon produced using iodine number method.

4. Use activated carbon for Adsorption and treatment of organic phenolic contaminant in water.
5. To study optimal condition of adsorption process.
6. Effects of pH, temperature, contaminant concentration, activated carbon dosage and time of contact will be studied.
7. To study adsorption at equilibrium and kinetic models.

## **Chapter Two**

### **Background**

#### **2.1 phenol and phenol derivatives**

##### **2.1.1 Properties of phenolic compounds**

Phenols are compounds of general formula Ar-OH. It's generally named as derivations of the simplest member of the family, phenol, C<sub>6</sub>H<sub>5</sub>OH. There are many forms of phenol due to the groups which attached to the ring and some of these given special name as methyl phenols which called cresol.

Phenols are resemble alcohols by containing –OH group and can be converted into ethers and esters but phenols differ from alcohol in having the –OH attached directly to an aromatic ring so it fairly acidic and in this become more acidity than alcohol and less than carboxylic acid. In most of their properties, however, and in their preparation, the two kinds of compounds differ so greatly that they deserve to be classified as a different family.

Phenolic compounds can form hydrogen bonding so simplest phenol are liquid and soluble in water. Unless some group capable of producing color, phenols themselves are colorless [4].

##### **2.1.2 Sources of phenolic compounds**

Phenolic compounds founded naturally especially in plant kingdom. Plants oils contain some phenolic compounds and we can isolated it from these plants as oil of cloves, oil of nutmeg, oil of vanilla bean, oil of olives,....etc. Waste water of agro industrial activities contains phenolic compounds that are capable to reach to the resources of water. This

industry related to the manufacturing win, spirits, and olives oil that's very common in Mediterranean region, so phenol like compounds are usually target for adsorption studies due to their presence in many water environments and their affinity with activated carbon surface [5].

There are many Industrial resources of phenolic compounds. Nearly all phenol is made today, however, by process that start with cumene, isopropylbenzene. Cumene is converted by air oxidation into cumene hydroperoxide, which is converting by aqueous acid into phenol and acetone.

Certain amount of phenol; as well as the cresols, is obtained from volatile and aqueous by-product material produce when convert coal into coke in the absence of air which called coal tar [4].

### **2.1.3 Phenol compounds uses and adverse effect**

Phenols rank near the top of the list of synthetic aromatic compounds [4].

Parent compound phenol use as an disinfection and for chemical syntheses.

Other classes of phenol can be use in chemical industry, wood processing, plastic processing, antioxidant, fungicide, PH indicators [6].

Phenolic compounds can be toxic to human and other organism especially for aquatic life. Phenol is one of the most uses of phenolic compound and more hazardous polluting, which can exert adverse effect on different biological process. It is considered one of the compounds that produce unpleasant taste and odor for drinking water and obstacles uses of waste water. The other important polluting phenolic compounds are p-nitro phenol, which is known to be persistent, bio accumulative, and high toxic.

It can enter the human body through all routes and its toxic action is much like that of aniline. P-nitro phenol aids the conversion of hemoglobin to methamoglobin, which is caused by the oxidation of iron (II) to iron (III) with the result that the hemoglobin can no longer transport oxygen in the body. Therefore, the complete removal of PNP or in some cases reduction of its concentration in wastewaters to an acceptable level has become a major challenge [7].

Chlorophenols are the most common organic pollutants used widely in agriculture, industry and public health. The most important chlorophenols sources are wastewaters from pesticide, paint, solvent, pharmaceuticals, paper and pulp industries as well as water disinfecting process, so it's prescribed as priority pollutants by the US Environmental Protection Agency (EPA) due to their toxicity and adverse effects upon human. It is considered as one type of the most hazardous materials, they are carcinogenic, mutagenic and resistant to biodegradation [8-9].

#### **2.1.4 Phenols and Olive oil production**

Olive mill wastes are increasing especially in the Mediterranean region due to increase olive trees and demand of olives oil worldwide. Processing of olive oil in the Mediterranean region are major contributors of pollution in that area [10,13].

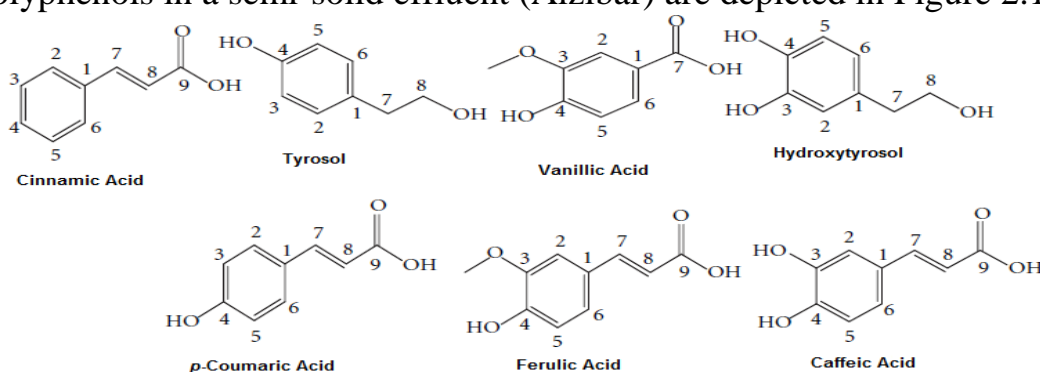
Production of olive oil consider as a polluting industry generate two types of waste: first; a semi-solid effluent (Alzibar), second; solid waste (Gift). The improper disposal of these wastes cause negative impact to air, water and soil. Olive mill wastes can cause pollution to water bodies which

affects the water color, appearance of an oily shine, and increase oxygen demand. Soil also affected with Olive mill wastes by change it is quality, toxic to plant life, and bacteria, and create odor nuisance when disposed into the soil.

Two-phase olive mill waste or semi-solid effluent rich in contaminating polyphenols is produced in large amounts by the industry of olive oil production [10-13].

Polyphenols (phenolic compounds) include many organic substances that have the common characteristics of possessing an aromatic ring with one or more substitute hydroxyl group and a functional chain. More than 30 phenolic compounds have been found in a semi-solid effluent (Alzibar)

Tyrosol and hydroxytyrosol are the most abundant polyphenols present in a semi-solid effluent (Alzibar). Other groups of polyphenols are also found in a semi-solid effluent (Alzibar), like cinnamic, caffeic, p-coumaric, vanillic and ferulic acids. These compounds are contributing to the toxicity and antibacterial activity of a semi-solid effluent (Alzibar) which limit its microbial biodegradability [14]. The structures of the most abundant polyphenols in a semi-solid effluent (Alzibar) are depicted in Figure 2.1.



**Fig 2.1: Most common phenolic compounds in semi-solid effluent (Alzibar) [15].**

### 2.1.5 Phenol removal

The efficiency of traditional biological treatment method to remove phenolic compounds is not satisfying due to stabilization and toxicity of some of these compounds as chlorophenol's. Besides, they also display a pronounced undesirable effect in potable water at concentration as low as 0.1 mg/l [12].

Composting method used widely to dispose of olive husk. It is anaerobic process in which microorganisms, under optimum conditions, biodegradable organic contents present on the olive waste. This process reduces levels of phenol compounds and lipids [10,11,13].

## 2.2 Cypress

### 2.2.1 Cypress classification

Cypress one of coniferous trees which evolve also fir, pin, and hemlock.

Conifers adapt to growth in many biomes around the world. Some are the Earth's largest plant and many species of cypress adapt to growth around the world which is different with size, tall and fruits [16].

Mediterranean cypress fruits carbons are the scope of this study to use for environmental cleanup. The scientific name of Mediterranean cypress called **Cupressus sempervirens**. The species name *sempervirens* comes from the Latin for 'evergreen'. It has other name depending on the region as Italian cypress. The Mediterranean Cypress is also known as the "drama tree" because of its tendency to bend with even the slightest of breezes [16-17].



### 2.2.2 Cypress properties

Japanese researcher discovered that charcoal produced from conifers wood as Japanese cypress (*C. obtusa*) and Japanesecedar (*C. japonica*) has great adsorption power, superior to that of commercially available activated carbon. Particularly when it comes to adsorbing from drinking water small quantities of chloroform and trichloroethylene (which have recently become an environmental problem) such charcoal is superior to the latest forms of fibrous, activated carbon both in terms of adsorption capacity and adsorption rate [18,19].

Cypress is the major natural resource of the Northern Hemisphere and consider the most commercially of tree species valued for their timber [19]. The Mediterranean Cypress is a species of cypress native to the eastern Mediterranean region, Syria, Lebanon, Palestine, Malta, Italy, western Jordan, ...etc. It can also be grown successfully in areas with cooler, moister summers, such as the British, New Zealand and the Pacific Northwest (coastal Oregon, Washington and British Columbia). It is also planted in United State as south Florida. It is a medium-sized coniferous evergreen tree to 35 m tall, with a conic crown with level branches and variably loosely hanging branchless. It is very long-lived, with some trees reported to be over 1,000 years old. The female seed fruit long, 25-40mm. it begin with green at first, maturing brown about 20–24 months after pollination The male cones are 3–5 mm long, and release pollen in late winter [18-20].

## **2.3 Adsorption**

### **2.3.1 Adsorption definition**

Adsorption is attachment or concentrates fluid particles to pore on surface, but absorption is taken fluid molecules by liquid or solid and distribution throughout them. The substance that adsorbs is the adsorbate and the underlying material is the adsorbent or substrate. The process of adsorption involves separation of substance from one phase accompanied by its accumulation or concentration at the surface of another. Separation occurs due to differences in molecular weight, shape or polarity. These differences cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. The reverse of adsorption is desorption [21].

### **2.3.2 Adsorption mechanism**

The molecules and atom can attach to the surface in two ways. First; physisorption (an abbreviation of, physical adsorption). In this way interaction due to Vander Waals interaction between the adsorbate and adsorbent. The energy of physisorption is very low (20 kJ/mole) due to weak of Vander Waals interaction. Second; chemisorption (an abbreviation of, chemical adsorption). The particles attached to the surface by forming covalent bond. The enthalpy of chemisorption is very much greater than physisorption which energy region 200 kJ/mol [22]. Table 2.1 summarizes the main differences between both processes.

**Table (2.1): Characteristics of chemisorption and physical adsorption [23].**

<b>Physical adsorption</b>	<b>Chemisorption</b>	<b>Characteristic</b>
In the region of 20 KJ/mol "exothermic"	In the region of 200 KJ/mol "endothermic"	Adsorption enthalpy ( $\Delta H$ )*
Dipolar interaction	Donor-acceptor complex	Bonding
Possible	Impossible	Adsorbate recovery

### **2.3.3 Factors affecting adsorption equilibrium**

There are several factors affecting the adsorption equilibrium. First, the characteristics of the adsorbent including surface area, pore size distribution, adsorbent dose and surface chemistry play an important role in the adsorption process. Second, the solubility of the adsorbate that consider the key factor affecting the adsorption capacity. In general, the adsorption increases with the decrease of adsorbate solubility [24]. Third, competitive adsorption of multisolute system may affect the adsorption of a certain constituent from liquid phase. This depends upon the strength of adsorption of the competing molecules, the concentrations of these molecules, and the type of activated carbon. Fourth, temperature effect on adsorption is variable; increase in temperature decreases physical adsorption as adsorbate molecules becomes in an energy level that overcomes weak van der Waals forces with the adsorbent. On the contrary, increase of temperature increases chemisorption [23].

Carbon surfaces dislike any form of charge. Water is highly charged (ionic) relative to the majority of organic molecules so the carbon would prefer the organic to be adsorbed [25].

Finally, adsorption process affected with pressure and molecular weight, both factors related directly with adsorption.

#### **2.3.4 Adsorption to remove phenolic compounds**

Adsorption process is one of the methods that used to remove contaminants from water. Other conventional processes for removing phenolic compounds include extraction, steam distillation, bacterial and chemical techniques, oxidation with ozone/hydrogen peroxide ion-exchange electrochemical oxidation reverse osmosis and photo catalytic degradation. Among the unit operations in water and waste water treatment, adsorption technique remains widely preferred due to its simplicity of design and operation initial cost, flexibility and, ease of operation and insensitivity to toxic pollutants. Moreover, adsorption does not result in the formation of harmful substances [26].

In adsorption technique activated carbon used as a powder to remove contaminants from water and consider as adsorbent. Langmuir and Freundlich model used to evaluate the adsorption capacity of some phenolic compounds by batch studies or system [27].

Activated carbon prepared from different abundant agriculture waste has been used in phenol removal from aqueous solutions. Table 2.2 summarizes some of agricultural waste for phenol removal.

**Table 2.2 : Activated carbon adsorbents from agricultural solid waste**

Reference	Constituent	Precursor
(Ekpete <i>et al.</i> , 2011)	Phenol	Fluted Pumpkin Stem
(Asma Abidin,2009)	Phenol	Decanter Cake
(Samar K. Dhidan,2012)	Phenol and PNP	Date Stones
(Azam <i>et al.</i> , 2008)	Phenol	Coconut Shell
(Saeedi <i>et al.</i> , 2009)	Phenol	Almond and Walnut Shell
(Moreno <i>et al.</i> , 1995)	Phenol Compounds	Bituminous Coal

### 2.3.5 phenol adsorption mechanism

The adsorption capacity of phenol onto activated carbon is dependent on the surface area, pore structure as well as surface chemistry of the activated carbon. Adsorption of phenol is highly sensitive to microporosity of activated carbon [28].

The structure of phenol solute can be divided into two groups the –OH group and the aromatic ring  $\pi$  electron system. The surface of activated carbon is described as a collection of organic functional groups containing oxygen. These groups take place at the edges of broken graphite planes, and basal planes consisting of large fused aromatic ring systems in a graphite-like structure [29].

Adsorption of phenol on activated carbons is a combination of two types of adsorption (chemical and physical). Dispersive interactions take place between the aromatic part of the phenol and the carbon's basal planes, so-called " $\pi$ – $\pi$ ", where chemical bonding is happening between the -OH group of phenol and the carboxylic groups on the carbon surface, so-called donor–acceptor complex" obtained a transition of physical and chemical adsorption in the study of phenols adsorption onto macroreticular resins

[30] . Chemisorptions takes place only at oxygen free site at the edges of active carbon sites while physical adsorption is happening all over the surface. Adsorption is highly affected by carbon surface oxygen group where the process is partially irreversible with high adsorption energies indicating strong bonding between carbon oxygen group and phenol [31]. There is a strong donor-acceptor complex between phenol and oxygen groups on carbon surface. The carbonyl oxygen, which has a larger dipole moment compared to carboxylic acid oxygen and acts as an electron donor, is responsible for the strong donor acceptor complex [32]. There is a reversible behavior of these complexes because of the pi-system interaction and phenol adsorbed in the planar orientation of activated carbon [33].

Coughlin and Ezra, 1968 showed that the oxidation of the carbon surface increases the amount of strongly acidic oxygen containing functional groups through the oxidation of carbonyl groups. These acidic groups results in the decrease of adsorption of phenol on activated carbon [29].

For different phenolic compounds studied, the value of the amount of adsorption at equilibrium increase in the following order:

m-aminophenol < p-cresol < phenol < PNP < m-chlorophenol

This order seems to be related to the electron-withdrawing or electron-donating properties of the substituents of the phenol compound. Thus, the electro-donating property of the substituents decrease in the above order, which goes from a very powerful electron-donating group on the benzene ring, such as the  $\text{-NH}_2$  group, to the electron-withdrawing group such as  $\text{-NO}_2$  or  $\text{-Cl}$ . Therefore, the electron-withdrawing favor the formation of

electron donor-acceptor complexes between these rings and basic groups on the surface of the AC [2].

## **2.4 Activated carbon**

### **2.4.1 Historical use of activated carbon**

AC use extended far back into history for water purification. Old Egypt use AC as purifying agent. In 1901, scientist developed ways to synthesize AC from coal, then AC introduce in industry in the first part of the previous century, when AC from vegetable material was produced for use in sugar refining. Since then, AC has been used in many industries [34].

### **2.4.2 Activated carbon definition**

Activated carbon is crystallizing form of group of substances with high surface area and large internal pore structure that make suitable for adsorbing and absorbing use. It is consider the most popular and cheapest material used in purification of alcohol and much of activated carbon is regenerated by desorption process to be used again hundreds, or even thousands, of times [35].

Activated carbon plays an important role in many areas of modern life such as removal the contaminant from water and air, and catalysis. Many research have appeared in literature to convert some agricultural and forest residues into activated carbon through physical or chemical activation process. Activated carbon produced from many resources as; coal, wood char, and agriculture by-product. The amount of agricultural and forest resources estimated that 129 and 176 million dry tones are available around the world [36]. This huge amount help environmental manager to

environmental remediation by converting these resources to the form that help to remove some contaminant.

We can classify agricultural by-product into two groups. Soft, compressible product of low density such as rice husk, peanut shells, soybeans, etc; and hard, dense and not easily compressed agricultural by-product such as pecan or walnut shells, and stones from dates, apricot or cherries [37]. Cypress cone can be classified as hard, dense and not easily compressed agricultural by-products.

A number of research's have been reported in the literature using coconut shell and palm kernel shell as a raw materials. Table 2.3 summarizes various works with reference to the raw materials, using, method of activation and their application of activated carbon produced [38].

**Table 2.3: Summary of earlier work on activated carbon using coconut shell and palm shell [38].**

Authors	Year	Raw materials	Method	Application
Lua and Guo	2001	Oil palm stones	CO <sub>2</sub> activation	Removal SO <sub>2</sub>
Hu and Srivinasan	2001	Coconut shell and palm shell	ZnCl <sub>2</sub> activation and CO <sub>2</sub> activation	Removal Phenol methylene blue
Guo and Lua	2003	Palm shell	H <sub>3</sub> PO <sub>4</sub>	Ammonia adsorption
Mozammel et al	2002	Coconut shell	ZnCl <sub>2</sub> activation	Iodine adsorption
Hu et al	2001	Coconut shell and palm seed	ZnCl <sub>2</sub> activation	Phenol and dye adsorption
Daud and Ali	2004	Palm shell and coconut shell	Physical activation (N <sub>2</sub> gas)	Nitrogen adsorption



### **2.4.3 Activated carbon properties**

#### **2.4.3.1 Introduction**

The properties of activated carbon depend on many factors as: characteristic of raw starting material, activation agent, type of activation process [39].

Activated carbon fall into two distinct classes, first one is graphitizing which is activated naturally under high temperature and pressure under the layer of sediment. Second is non-graphitizing which derived from biomass under artificial condition.

Many methods used for removing pollutants from wastewaters such as: ion exchange, evaporation, adsorption...etc. Most of these methods suffer from some problem, as cost or residual metal sludge. Activated carbon has the potential adsorbents for the removal of heavy metals and other contaminants from industrial wastewater because low cost, high surface area and micro porous character [40].

The amount and characteristic of the char which contain activated carbon vary according to two main factors:

1. The plant factor which depend on: plant species, location within plant, and growth conditions.
2. Combustion environment [41].

#### **2.4.3.2 Factors affected the properties of activated carbon during preparation**

Knowledge of the effects of different variables during carbonization and the activation process is important in controlling the porosity of the final

product [42]. Among these parameters are temperature, impregnation rate, activation time and nitrogen flow that are discussed below:

### **Activation temperature**

Characteristics and microstructure of wood charcoal change dependently upon the carbonization conditions. It was found that increase of the carbonization temperature developed formation of micropores of the charcoal. The crystal structure of the charcoal remarkably changed in the temperature range between 600°C and 800 °C [43].

The temperature applied during carbonization/ activation process plays a major role in the development of porous structure. Higher temperatures increase the surface area due to widening of macropores of the precursor to a point further increase in the temperature causes massive destruction of micropores [44]. On the other hand, the increase in activation temperature leads to decrease in the yield of activated carbon produced due to the loss of volatile materials. A minimum heating rate of 10 °C/ min is optimal to guarantee effective nitrogen diffusion inside the precursor and enhance the removal of volatile organic compounds. Higher heating rate causes partial graphitization of the precursor which has a negative impact on the surface area of the activated carbon produced [45].

### **Activated agent concentration and Impregnation ratio**

The phosphoric acid  $\text{H}_3\text{PO}_4$  activating agent acts as a catalyst on the carbon surface of the precursor. The concentration of phosphoric acid  $\text{H}_3\text{PO}_4$  has influenced significantly the adsorption ability of the samples. Phosphoric acid  $\text{H}_3\text{PO}_4$  concentration appears to be key factor effecting iodine

adsorption of the prepared AC in its range of 40 – 80% and the maximum adsorption capacity with concentration 50%. Phosphoric acid  $\text{H}_3\text{PO}_4$  promotes the pyrolytic decomposition of the starting material and the formation of cross-linked structure, the decomposition is promoted by the catalytic effect of  $\text{H}_3\text{PO}_4$  on the bond cleavage reactions but the cross-linked phenomenon is due to interaction between  $\text{H}_3\text{PO}_4$  and biomass in the precursor leading to formation phosphate linkages between the fragments in the biomass [46].

Impregnation ratio between Phosphoric acid  $\text{H}_3\text{PO}_4$  and raw material of AC appears to be low affecting iodine adsorption and yield of AC produced and the best ratio is 2:1[46].

### **Nitrogen flow rate**

The aim of introducing nitrogen flow during the carbonization/ activation process is to guarantee oxygen-free atmosphere inside the furnace; preventing the burn off (oxidation) of the precursor. Low nitrogen flow rate (0.2-0.5 l/min) is recommended for the development of high surface area activated carbon [47]. Higher nitrogen flow rate may lead to decrease in surface area as it lowers the diffused temperature inside the carbon structure of the precursor.

### **Activation time**

There is a significant impact of pyrolysis holding time on the surface area, total pore volume and pore size distribution of activated carbon. It has been reported that longer hold time results in higher surface area, total pore volume and microporous volume [45]. The major increase in surface area

and total volume occurs between 30 min and 1 hr. Longer holding time increases the surface area but with less extent. These trends can be explained by the fact that carbon gasification is enhanced by the increased holding time, thus causing the removal of carbon atoms on pore walls, which widened the micropores [48].

#### **2.4.4 Methods of carbon activation**

##### **2.4.4.1 Physical activation**

Physical activation achieved most frequently by burning off agricultural by-product rich with carbon in an oxidizing environment to produce activated carbon. The usual commercially choices of activation gas are steam, CO<sub>2</sub>, air, or their mixtures [49].

The physical activation process involves two steps: the first one is the carbonization (so-called pyrolysis) of the carbonaceous precursor at elevated temperatures (500-1000°C) under inert atmosphere in order to eliminate oxygen and hydrogen elements as far as possible. The second stage involves thermal activation of this char. This can be done at the same temperature [50].

##### **2.4.4.2 Chemically activation**

Chemically activation is principally used for the activation of wood-based activated carbon and activated carbon from stones e.g., olive stones. It gives crystalline plates with very open pore structure, which is ideal for adsorption of large molecules [51].

Chemical activation of carbon carried out simultaneously by mixing the raw material with chemicals such as phosphoric acid, potassium hydroxide,

or  $\text{ZnCl}_2$ . These chemicals are added to enhance carbonization, resulting in improved development of the pore structure [39].

Recently, chemical activation has been shown as an efficient method to obtain activated carbons with high surface area and narrow micropore distribution [51].

Activation agent,  $\text{H}_3\text{PO}_4$  is widely used in the preparation of activated carbons from lignocellulosic products and offers some advantages such as non-polluting character and ease of elimination by extraction with water [46].

Moreover,  $\text{H}_3\text{PO}_4$  inflicted physical and chemical modifications on the botanical structure by penetration, particle swelling, and partial dissolution of biomass, bond cleavage and reformation of new polymeric structures resistant to thermal decomposition [52].

In this study cypress fruits will be utilized as a raw material for the production of activated carbon with different particles size. Chemical activation will be performed using  $\text{H}_3\text{PO}_4$  as activation agent.

#### **2.4.5 application of activated carbon**

AC is widely use in industries and environment clean up. Examples of its usage:

1. Water treatments in removing phenol compounds, halogenated compounds and other harmful pollutants.
2. Air purification in removing some volatile organic compounds, sulfur oxide and nitrogen oxide.
3. Purification of many chemical, food and pharmaceutical products.

#### 4. Recovery of industrial solvents.

##### **2.4.6 conclusion**

Because of their wide usage of AC in industry and environment cleaning, the demand of AC is increasing year by year. Commercial AC is quite expensive. The world now seeks for the cheapest AC derived from agricultural waste or residual. Many activated carbon raw material used. The Japanese scientist discovered that charcoal produced from conifers wood as Japanese cypress (*C. obtusa*) and Japanese cedar (*C. japonica*) has great adsorption power, superior of commercial available AC to treatment of wastewater and waste gas [19]. The Japanese adsorption experiments proved that a promising abundant, low cost and high capacity adsorbent for the removal contaminants

In this research properties of Mediterranean cypress fruit activated carbon investigated. This AC produced through chemical activating process using activating agent ( $\text{H}_3\text{PO}_4$ ). Many parameters studied as the activation conditions, CFAC characterization, batch experimental adsorption study for the PNP to explain the mechanism of adsorption by applying many models and study the factors affected the adsorption process.

## Chapter Three

### Experimental Work

#### 3.1 Materials

**3.1.1 Precursor:** Cypress fruit were used as the precursor in the preparation of activated carbon. Dried cypress fruit were collected from the cypress trees near Nablus area, crushed using moulinex device, and sieved. Only the fractions of particle sizes comprised between 0.3mm to 1.4mm were selected for the preparation of activated carbon.

**3.1.2 Activators:** Phosphoric acid  $H_3PO_4$  of purities 98% were used as chemical reagents for activation of cypress crushed fruit.

**3.1.3 Adsorbate:** P-nitrophenol of purities higher than 97% were used as adsorbate in this study.

**3.1.4 Chemicals:** All other chemical used such as hydrochloric acid, sodium thiosulfate, iodine and sodium hydroxide were of analytical grades.

**3.1.5 Furnace:** Tubular regulated furnace (Lindberg 9001) with a 0.25 cm thick cylindrical stainless steel tube (4 cm inner diameter and 74 cm length).

**3.1.6 UV-visible spectrophotometer :** To determine the PNP concentration UV-visible spectrophotometer Shimadzu UV-160A used.

#### 3.2 Preparation and characterization of activated carbon

To prepare activated carbon from crushed cypress fruit different chemical reagents were used. Phosphoric acid solution (450 mL, 50% w/w) was used in chemical activation of cypress fruit. This concentration was reported in literature to give the best surface area for carbon activated by phosphoric

acid  $\text{H}_3\text{PO}_4$  [53]. The solution was added to the crushed cypress fruit sample and the mixture was left for 24 h at room temperature.

After this impregnation procedure, the solution was filtered to separate the residual acid. The crushed cypress fruit then washed several times with deionized water, dried in an oven at  $110^\circ\text{C}$ , before carbonization at  $700^\circ\text{C}$  with constant rate increase of  $10^\circ\text{C} / \text{min}$  for 1h under inert atmosphere ( $\text{N}_2$  gas 99.9%) at a flow rate of  $(0.5 \text{ L min}^{-1})$ . At the end of activation time the carbonized samples were withdrawn from the furnace and allowed to cool to room temperature under the same nitrogen flow. The samples were repeatedly washed with deionize water. After that, the samples were dried at  $110^\circ\text{C}$  for 24 h. Finally the samples were stored in covered beaker inside desiccator for further use.

### **3.3 Characteristics of prepared activated carbon**

The prepared CFAC was characterized by selected physical properties including percentage yield, bulk density and surface area using iodine number method, chemical properties including ash content, pH and conductivity, and adsorption properties including PNP and iodine adsorption.

#### **3.3.1 Yield of activated carbon**

The crushed cypress fruit sample weighted before carbonization and after carbonization, and then the yield of the activated carbon was estimated from the following equation:

$$\text{yield of activated carbon}(\%) = \frac{W_a}{W_b} \times 100 \quad (3.1)$$



Where  $W_a$  is the weight of crushed cypress fruit sample after carbonization,  $W_b$  is the weight of crushed cypress fruit sample before carbonization.

### 3.3.2 Dry density

Dry density is a measure of the weight of the material that can be contained in a given volume under specified conditions. The volume used in this determination includes, in addition to the volume of the skeletal solids. A 10 ml crocked density cylinder was weighed then was filled to a specified volume with CFAC that had been dried in an oven at 80 °C for 24 h then the cylinder reweighed [54]. The dry density was then calculated as follows:

$$\text{dry density} = \frac{W_c - W_e}{V_c} \times 100 \quad (3.2)$$

Where  $W_c$  is the weight of cylinder and CFAC (g),  $W_e$  is the weight of empty cylinder and  $V_c$  is cylinder volume packed with dried activated carbon (ml).

### 3.3.3 Ash content

The ash content of an activated carbon is the residue that remains when the carbonaceous portion is burned off. The ash content of CFAC was determined by standard methods [55].

A crucible was preheated in furnace, cooled and weighed then 0.5 g of CFAC was dried at 80 °C for 24 h transferred into weighted ceramic crucible and reweighed. The samples were heated in an electrical furnace at

650°C for 3 h. Then the crucibles were cooled to room temperature and weighed. The percent of ash was calculated as follows:

$$\text{ash content(\%)} = \frac{W_{S3} - W_{S2}}{W_{S1}} \times 100 \quad (3.3)$$

Where  $W_{S3}$  is the weight of crucible containing ash (g),  $W_{S2}$  is the weight of crucible (g), and  $W_{S1}$  is the weight of original CFAC used (g).

Volatile matter percentage can be calculated using the equation.

$$\text{volatilematter(\%)} = \frac{\text{weight of volatil component}}{W_{S1}} \times 100 \quad (3.4)$$

Weight of volatile component can be calculated using the equation.

$$\text{weight of volatilecomponent(g)} = W_{S1} - [W_{S3} - W_{S2}] \quad (3.5)$$

### 3.3.4 Moisture content

Thermal drying method was used in the determination of moisture content of CFAC [56]. A 0.5 g of CFAC was placed into weighed beaker. The samples were dried at 110°C to constant weight for 4h. Then the samples were cooled to ambient temperature and weighed. The moisture content was calculated by the following equation:

$$\text{moisture(\%)} = \frac{W_{b2} - W_{b1}}{W_c} \times 100 \quad (3.6)$$

Where  $W_{b2}$  is the weight of beaker containing original sample (g),  $W_{b1}$  is the weight of beaker containing dried sample (g), and  $W_c$  is the weight of original sample used (g ).

### **3.3.5 pH measurement**

The pH value of prepared CFAC was determined by putting 1 g sample in 100 ml deionized water and stirring at 150 rpm for 1 h and the pH of filtrated solution were taken [57].

### **3.3.6 Conductivity measurement**

Electrical conductivity of CFAC was measured by using the method of Ahmedna et al. 1997 [58]. A 1 wt% solution of sample in deionized water was stirred at 150 rpm at room temperature for 20 min. Electrical conductivity was measured by electrical conductivity meter using micro siemens per meter ( $\mu\text{S/m}$ ) unit.

### **3.3.7 Iodine number**

Iodine number is the main parameter used to characterize of AC because it show the activity level and micropore content. Higher iodine number mean higher degree of activation.

Iodine number is defined as the milligrams of iodine adsorbed by one gram of activated carbon. Basically, iodine number is a measure of the micropore content of activated carbon (0 to 20 °A) by adsorption of iodine from solution. Iodine number of the prepared carbon was determined as follows: 10 ml of 0.1 N iodine solution in a conical flask is titrated with 0.1 N sodium thiosulfate solution in the presence of 2 drops of 1 wt% starch solution as an indicator, till it becomes colorless. The burette reading is

corresponding to  $V_b$ . Then weigh very accurately 0.05 g of activated carbon and add it to conical flask containing 15 ml of 0.1 N iodine solution, shake the flask for 4 min and filter it, then titrate 10 ml of filtrate with standard sodium thiosulfate solution using 2 drops of starch solution as indicator, now the burette reading is corresponding to  $V_s$ . The iodine number was then calculated by using the following equation [59].

$$IN = \frac{(V_b - V_s) \cdot N \cdot (126.9) \cdot (15/10)}{W_c} \quad (3.7)$$

Where IN is iodine number (mg/g),  $V_b$  and  $V_s$  are volumes of sodium thiosulfate solution required for blank and sample titrations (ml), respectively, N is the normality of sodium thiosulfate solution (mole/L), 126.9 g is atomic weight of iodine, and  $W_c$  is the mass of activated carbon used (g).

The surface areas of the prepared activated carbon was estimated through a calibration curve which has a correlation coefficient of 0.997 between the iodine numbers and BET surface area of some established activated carbons from the literature [60].

### **3.4 Adsorption experiments**

PNP adsorption onto activated carbon surfaces was studied by batch experiments. Experiments were conducted in a set of 100 mL capped conical flasks. All used apparatus were thoroughly precleaned with distilled water. After the addition of PNP solution to the activated carbon and, experiments flasks were shaken at 170 rpm using a temperature controlled

water bath (Tuttnauer) with shaker (Burell 75). The flasks were left under continued constant-speed shaking for the desired time.

#### **3.4.1 Stock solutions preparation**

A fresh PNP stock solution (1000 mg/L ) was prepared by dissolving a mass of 1.03 g PNP in 100 ml distilled water and diluted to 1000.00 ml scale in a volumetric flask. From this solution, different solutions (10-100 mg/L) were prepared by dilution. In each PNP adsorption experiment, an aliquot (50 mL) of these solutions was used. PNP concentration was analyzed at the end of each experiment. Each experiment was performed in duplicate using identical conditions.

#### **3.4.2 Effect of contact time (kinetic study)**

The effect of time on adsorption was studied. PNP solution (50 mL, 80 mg/L) was added to adsorbent sample (0.1 g) at pH 4. The mixture was shaken at 25°C. Aliquots (0.5 mL each) of the clear solution were pipette out at different time intervals until equilibrium was reached after 150 minute.

#### **3.4.3 Effect of adsorbent dosage**

Different amounts (0.02-0.3 g) of prepared activated carbons prepared from cypress fruit (CFAC) were placed into conical flasks, then solutions (50 mL, 80 mg/L PNP) were added to each flask and the pH was 4. The mixtures were then shaken for 150 minute at 25°C.

#### **3.4.4 Effect of temperature**

The effect of temperature on adsorption was studied. PNP solutions (50 mL, 80 mg/L each) were added to adsorbent samples (0.10g) at pH 4. The

mixtures were shaken for 150 minute at different temperatures in the range 15-45°C.

### 3.4.5 Effect of PNP concentration

In each adsorption experiment, PNP solutions of a given concentration ranging from 0 to 100 mg/L PNP was added to 0.10g adsorbent, with initial pH 4. The flasks were shaken at 25°C for 150 minute to reach equilibrium. The initial and final concentrations of PNP were measured.

The amount of adsorption at equilibrium,  $q_e$  (mg/g), was calculated by

$$q_e = \frac{(C_o - C_e) V}{W} \quad (3.8)$$

$$PR (\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (3.9)$$

Where PR percentage removal (%),  $C_o$  and  $C_e$  are the initial and equilibrium concentrations of PNP solution (mg/L), respectively,  $V$  is the volume of solution (L), and  $W$  is the weight of activated carbon used (g).

### 3.4.6 Adsorption equilibrium model

Adsorption equilibrium models are a good way to explain the adsorption system. It provides information about the adsorbate and adsorbent surface properties. There are several equilibrium isotherm models applied including, Freundlich, Langmuir, Tempkin....etc. These models developed to fit adsorption system with various condition [61].

However, the most important and used in the field of adsorption are Freundlich and Langmuir.

### 3.4.6.1 Langmuir equation:

To determine the maximum PNP adsorption capacity of prepared activated carbon, the experimental adsorption data obtained were fitted to the Langmuir isotherm model. It assumes a mono layer adsorption onto a uniform adsorbent surface with energetically identical sorption sites. Langmuir isotherm equation is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{qm} \quad (3.10)$$

Where  $q_e$  is the amount of PNP adsorbed per unit mass of activated carbon (mg/g),  $q_m$  is the maximum amount of PNP adsorbed per unit mass of activated carbon (mg/g),  $C_e$  is the equilibrium concentration of the PNP (mg/L), and  $b$  is the Langmuir constant (L/mg). The Langmuir isotherm model which is based on the assumption of a homogeneous adsorbent surface with identical adsorption sites has been successfully used by many researchers to correlate the experimental adsorption data of phenolic compounds on activated carbons [62].

### 3.4.6.2 Freundlich equation:

It describes equilibrium on heterogeneous surfaces and hence does not assume mono layer capacity [63]. The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

$$\log q_e = \log KF + \frac{1}{n} \log C_e \quad (3.11)$$

Where  $C_e$  is the equilibrium concentration of the adsorbate (mg/L),  $q_e$  is the amount of adsorbate per unit mass of adsorbent (mg/g),  $K_F$  and  $n$  are Freundlich constants.  $n$  giving an indication of how favorable the adsorption process is.  $K_F ((\text{mg/g}) (\text{L/mg})^{1/n})$  is related with adsorption capacity of the adsorbent. The slope  $(1/n)$  ranging between 0 and 1 is a measure of surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [64]. A value for  $(n)$  below one indicates a normal Freundlich isotherm, while  $(n)$  above one is indicative of efficient adsorption [65].

### **3.4.7 Adsorption kinetics**

Adsorption kinetics study is important, since they give information about the adsorption system behavior and the rate at which specific constituent is removed using certain adsorbent. In addition, they provide information about whether the adsorption process is chemical or physical and which specifically is the rate limiting step. There is several models that describe the adsorption process. In this research we will use adsorption reaction models, which are classified into four models.

#### **3.4.7.1 Pseudo-first order kinetic models**

A pseudo-first order kinetic model is considered the earliest models develop to the kinetic process of adsorption. The final integrated form equation of this model as follows:

$$\log(q_e - qt) = \log q_e - \frac{k_1}{2.303} t \quad (3.12)$$



Where  $q_e$  and  $q_t$  (mg/g) are the adsorption capacity at equilibrium and at time  $t$  (min), respectively.  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first order rate constant [66].

#### 3.4.7.2 Pseudo-second order kinetic models

This model employed to describe the adsorption of metal ion and polar functional group such as, ketones, aldehydes, dyes, herbicides, and phenolics compounds from aqueous solution assuming that Langmuir equation applies.

The linearized integral form of the model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3.13)$$

Where  $q_e$  and  $q_t$  (mg/g) are the adsorption capacity at equilibrium and at time  $t$  (min), respectively  $k_2$  is the rate constant ( $\text{g}/(\text{mg} \cdot \text{min})$ ) [67].

#### 3.4.7.3 Second order kinetic models

The typical form of second order rate equation can be applied to describe the adsorption process based on adsorbate uptake rate. The integrated forms of this equation as follow [68].

$$\frac{1}{C_t} = k_2^* t + \frac{1}{C_0} \quad (3.14)$$

Where  $C_0$  and  $C_t$  (mg/l) is the concentration of solute at  $t=0$  and at time  $t$  (min), respectively, and  $k_2^*$  ( $\text{L}/(\text{mg} \cdot \text{min})$ ) is the rate constant.

#### 3.4.7.4 Intra-particle diffusion model:

In a liquid-solid system, the theory proposed by Weber and Morris to link the fractional uptake of solute on particles varies proportionally with  $t^{1/2}$ . The Weber and Morris equation is:

$$qt = k_b t^{1/2} + A \quad (3.15)$$

$qt$  (mg/g),  $k_b$  (mg/g min<sup>1/2</sup>) is the rate constant of intra-particle diffusion and (A) gives an idea about the thickness of the boundary layer. The value of  $k_b$  will be calculated from the slope of plotting  $qt$  v  $t^{1/2}$  [69].

## **Chapter Four**

### **Results and Discussion**

#### **4.1 Characterization of cypress fruit activated carbon**

Activated carbon has unique characteristics; its high adsorption capacity is related to the porous structure and chemical characteristics. These characteristics determine its interaction with polar and non-polar compounds. It also has active edge sites that determine its chemical reaction nature. Therefore, the adsorption phenomena can't only be explained in relation to surface texture including surface area and pore size distribution, but a combination of both surface and chemical characteristics of activated carbon.

The direct viewing of the topography of the CFAC surfaces Figure 4.1 and Figure 4.2 show that the CFAC prepared seems to be fiber featured due to cellulose molecules activated with temperature and without pressure but bituminous coal form under temperature and pressure so it take granular shapes Figure 4.3



**Figure 4.1: Cypress fruit activated carbon**



**Figure 4.2: Magnified picture of cypress fruit activated carbon**



**Figure 4.3: Bituminous coal activated carbon [70]**

Figure 4.1 and figure 4.2 show the CFAC prepared which seem to be fiber feature due to cellulose molecules activated with temperature and without pressure but bituminous coal form under temperature and pressure so it take granular shapes Figure 4.3

Other properties of CFAC prepared were determined and summarized in Table 4.1. Ash content of CFAC equal 66 % and this value relatively high compared with commercial activated carbons which reach 17.1% [71].

Surface areas were measured using the iodine number method. The results show that the iodine number equal 494.9mg/g., this result resemble the result that reported an iodine number of Haimour and Emeish (2006) that

finds the iodine number of activated carbon prepared by chemical activation of date stones using phosphoric acid 495 mg/g [72].

We can use standard calibration curve for iodine number in Figure 4.4 to find surface area of activated carbon. The surface area calculated from the Figure 4.4 using curve equation that equal 524.1(m<sup>2</sup>/g) which enter the range of commercial AC surface area.

**Table 4.1: Characteristics of CFAC sample.**

Characteristic	Activated carbon
Yield of activation (%)	51.8
bulk density (g/ml)	0.472
Electrical conductivity(μs/m)	991
surface area (m <sup>2</sup> /g)	524.1
ash content (%)	66
Volatile matter (%)	44
moisture content (%)	7.4
pH	4
Iodine number (mg/g)	494.9

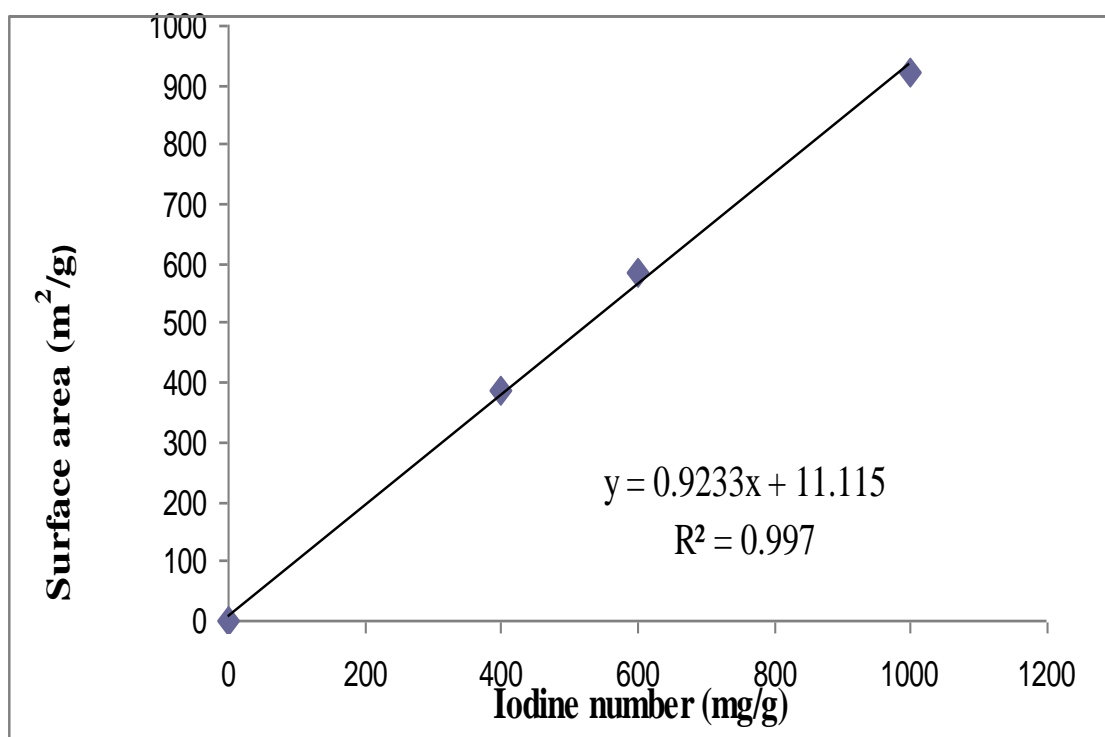
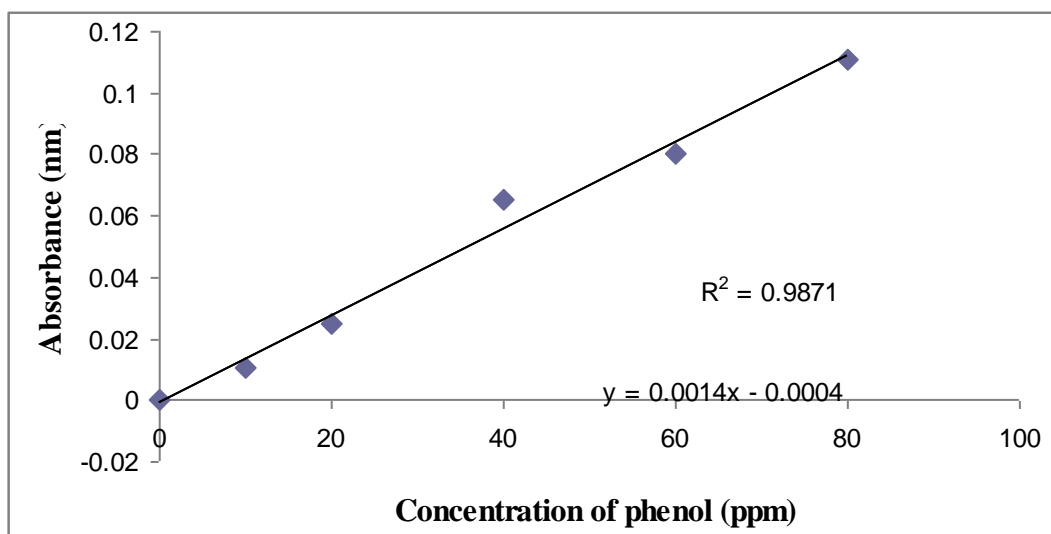


Figure 4.4: standard calibration curve for iodine number [7].

#### 4.2. Calibration curve for p-nitrophenol

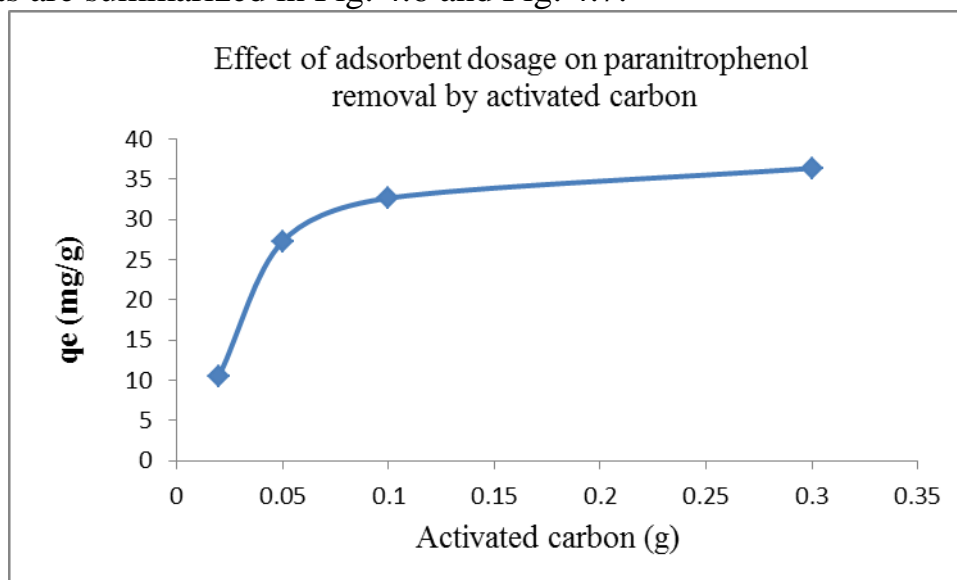
Stock solution was used to prepare different calibration standard solutions with concentrations 10, 20, 40, 60, 80, and 100 mg/L PNP. Then the samples PNP were analyzed by a UV-visible Spectrophotometer (Shimadzu UV-160A) at maximum wave lengths of 400 nm for PNP. Calibration curve were constructed by plotting value of absorbance vs. concentration of standard PNP as shown in in Fig. 4.5.



**Figure 4.5:** Calibration curve for PNP at 25°C.

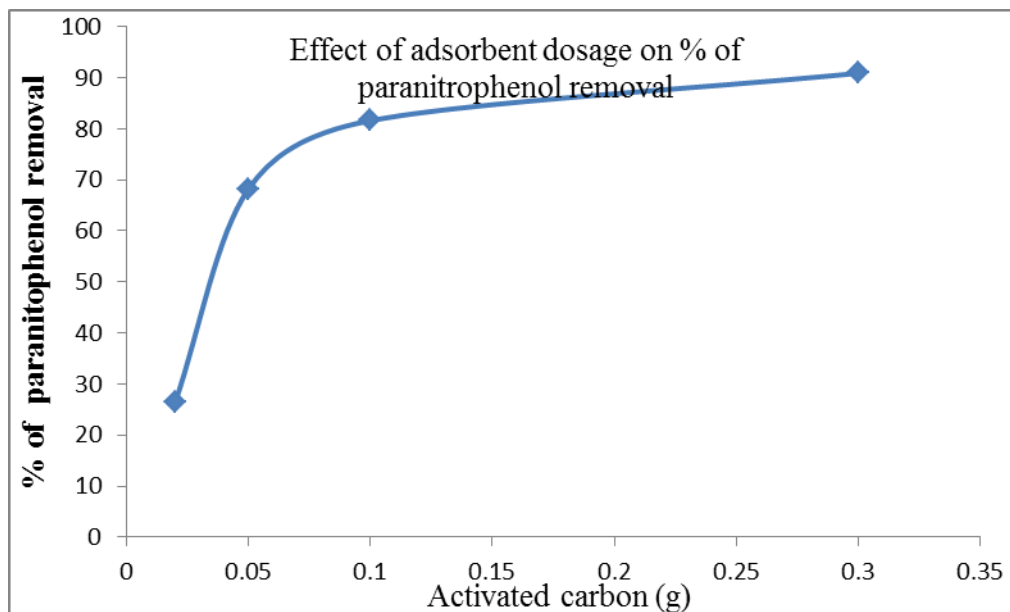
### 4.3 Effect of adsorbent dosage

The effect of CFAC dosage on PNP removal was studied, using 0.02 to 0.3g CFAC at an adsorption time of 150 min. to reach equilibrium. The results are summarized in Fig. 4.6 and Fig. 4.7.



**Figure 4.6:** Effect of adsorbent dosage on PNP removal by CFAC at (initial conc.,: 80mg/L, initial pH: 4, temperature: 25 ° C and contact time:150 min).



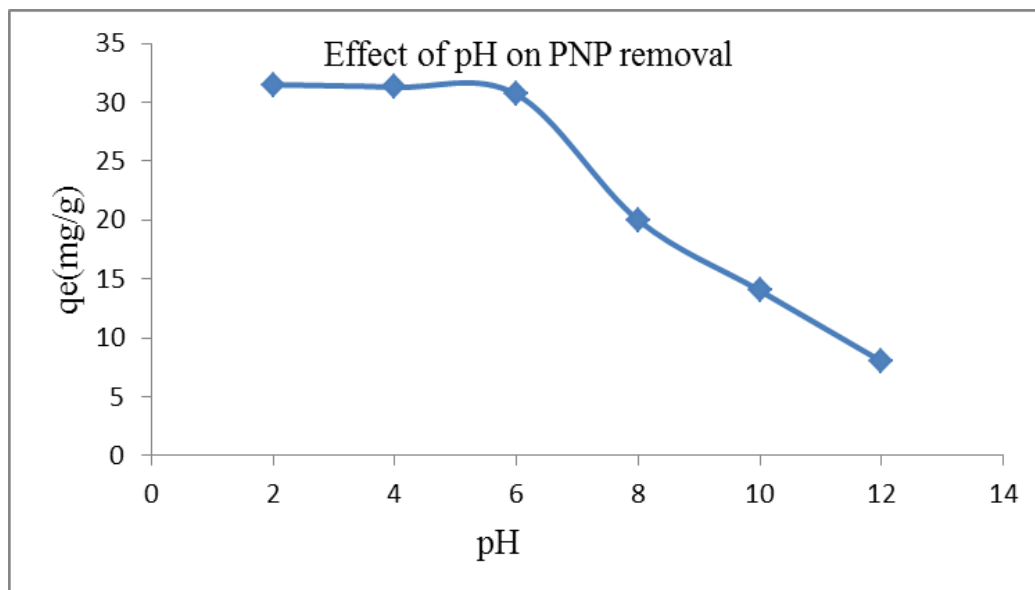


**Figure 4.7: Effect of adsorbent dosage on % of PNP removal by CFAC at (initial conc: 80mg/L, initial pH: 4, temperature: 25 °C and contact time:150 min).**

The percent of PNP removal increased by increasing adsorbent dosage. Adsorption increases up to 90.9 % with adsorbent dosage of (0.3 g/50 mL), because increasing adsorbent dosage at fixed PNP concentration provided more available adsorption sites and thus increased the extent of PNP removal.

#### **4.4 Effect of pH**

The variation of PNP adsorption onto CFAC was investigated in the pH range 2-12 using ammonium hydroxide to control pH. The effect of pH on PNP removal was studied, using 0.1g AC at an adsorption time of 150 min. to reach equilibrium. Figure 4.8 summarizes the results.



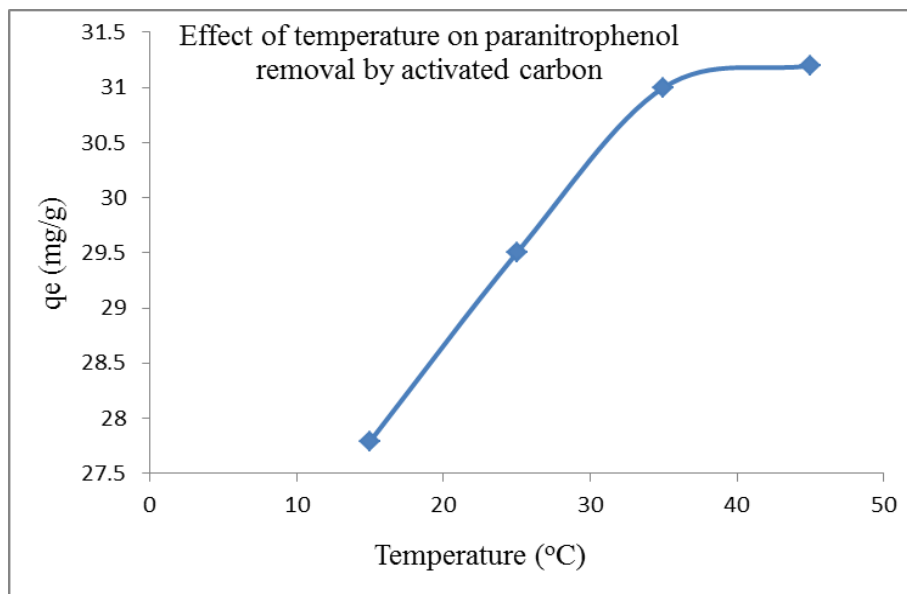
**Figure 4.8: Effect of pH onto PNP removal at (initial conc: 80 mg/L, temperature: 25 °C, contact time: 150 min and solid/liquid ratio 0.1 g/50 mL).**

At lowering pH from 6 to 2 the Figure shows that the PNP adsorbent increases slightly, but the decrease of adsorbent at pH from 6 to 12 is highly extreme.

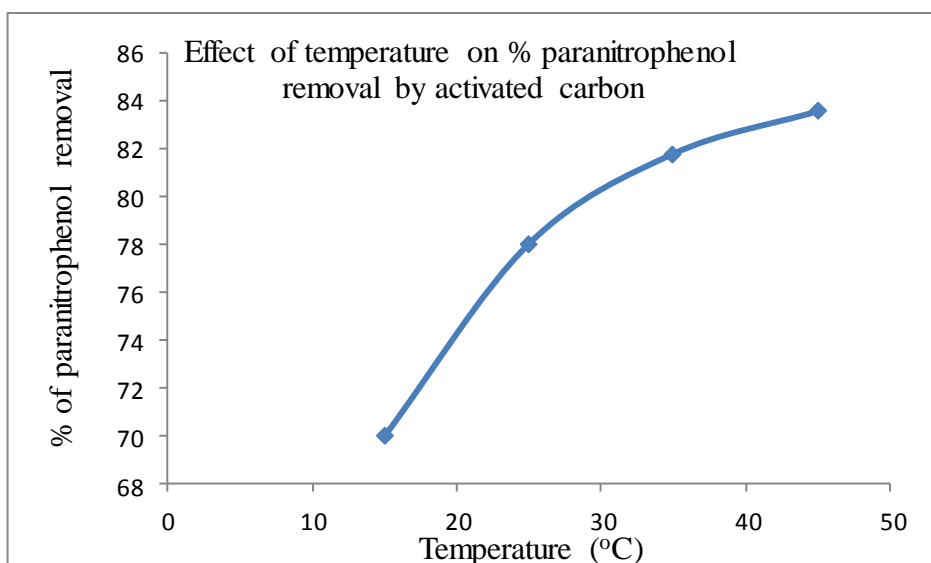
#### **4.5 Effect of Temperature**

The effect of temperature on PNP adsorption onto CFAC was investigated in the range 15-45 °C. The results are shown in Fig. 4.9 and Fig. 4.10.

The Figures shows that PNP adsorption increased with increase temperature. The highest percentage adsorption performance at 45 °C which reach to 83.58 %.



**Figure 4.9:** Effect of temperature on PNP removal by CFAC at (initial conc: 80mg/L, initial pH: 4, contact time: 150 min and solid/liquid ratio 0.10 g/50 mL).

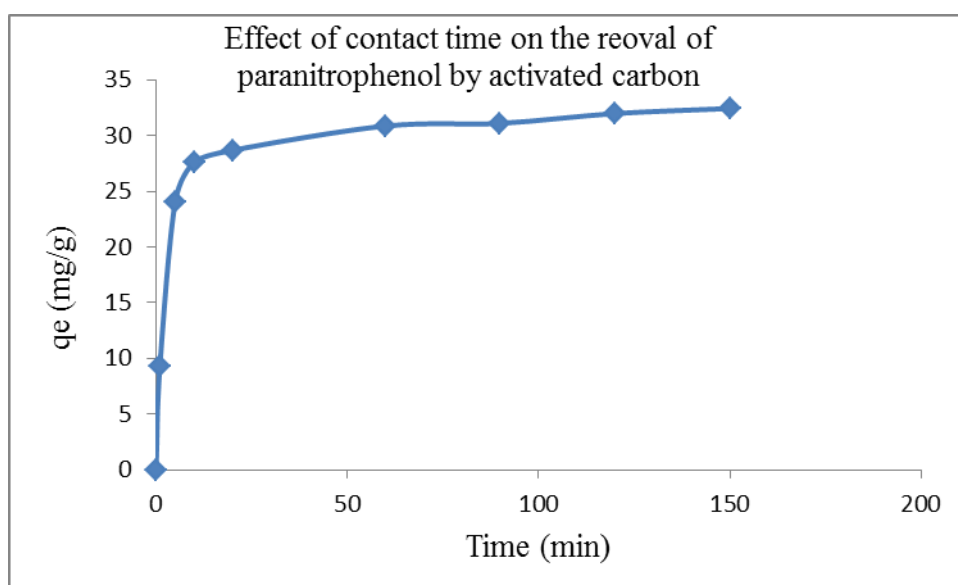


**Figure 4.10:** Effect of temperature on % PNP removal by CFAC at (initial conc: 80mg/L, initial pH: 4, contact time: 150 min and solid/liquid ratio 0.10 g/50 mL).

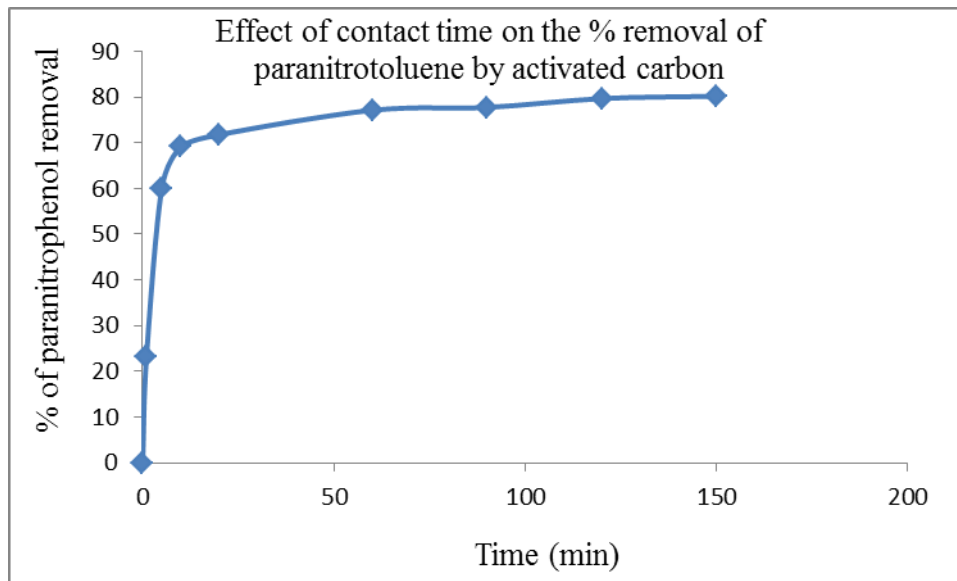
#### 4.6 Effect of Contact Time

The effect of contact time on adsorbed amount and removal percentage of PNP is shown in Fig.4.11 and Fig. 4.12, respectively.

The adsorbed amount of PNP onto CFAC increases with the increase of contact time, as shown in Fig.4.11 and Fig. 4.12, and the adsorption reached equilibrium in about 150 min. for PNP. For PNP adsorption, a rapid increase in adsorbed amount is achieved during the first 10 min. The fast adsorption at the initial stage may be due to the higher driving force making fast transfer of PNP to the surface of CFAC particles and the availability of the uncovered surface area and the remaining active sites on the adsorbent as mentioned by Aroua et al. [73].



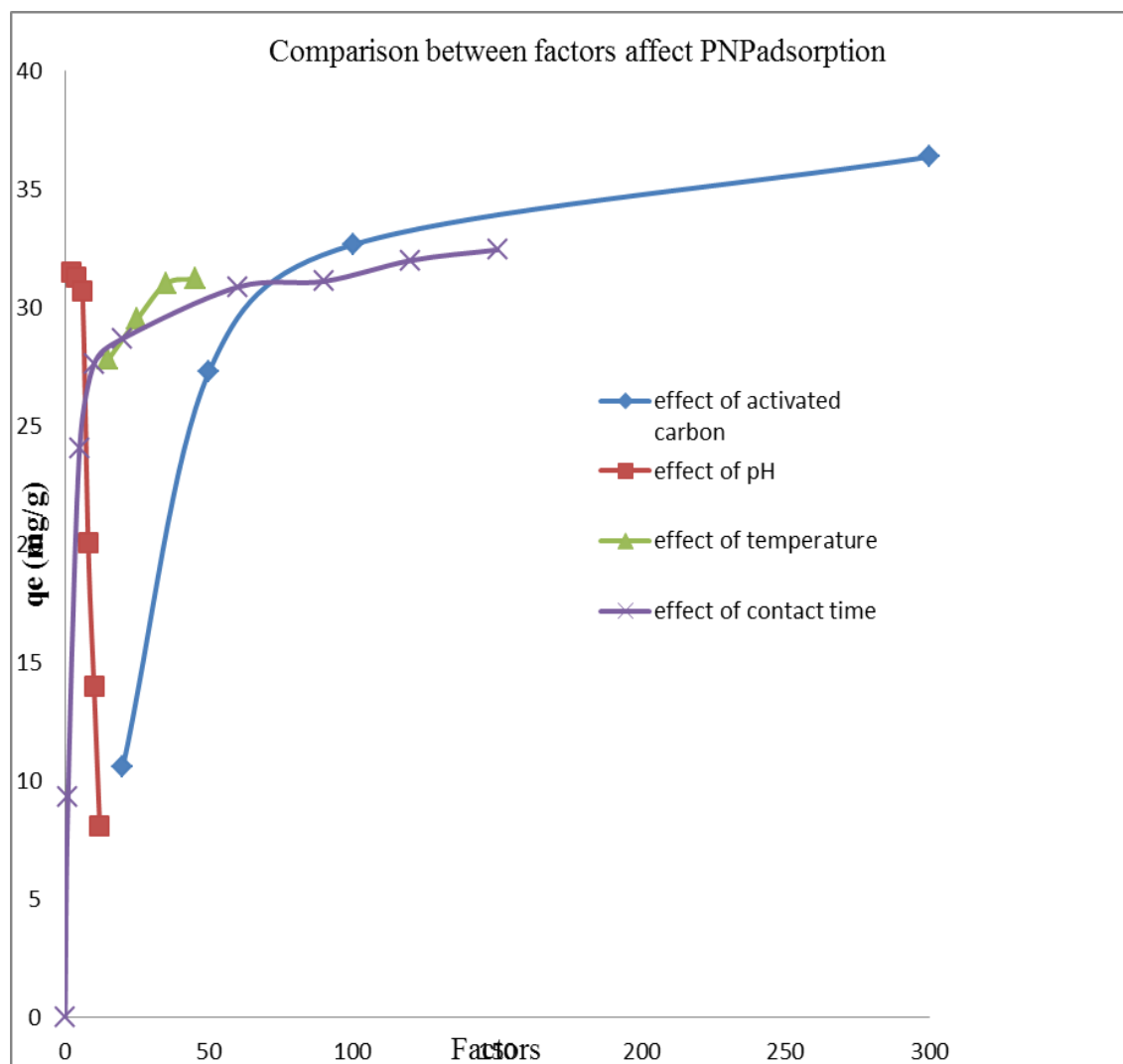
**Figure 4.11: Effect of contact time on the removal of PNP by CFAC at (initial conc: 80 mg/L, initial pH: 4, temperature: 25°C and solid/liquid ratio 0.1 g/50 mL).**



**Figure4.12: Effect of contact time on the percentage removal of PNP by CFAC at (initial conc: 80 mg/L, initial pH: 4, temperature: 25°C and solid/liquid ratio 0.1 g/50 mL).**

#### 4.7 determination of optimum conditions for PNP adsorption

The optimum conditions for PNP adsorption were carried out by plotting  $q_e$  vs. factors affected PNP adsorption Figure 4.13 and data in Tale 4.14.



**Figure 4.13:** Comparison between factors which affected the removal of PNP by CFAC at initial conc.: 80 mg/L.

**Table 4.2: Comparison between factors which affected the removal of PNP by CFAC at initial conc.: 80 mg/L.**

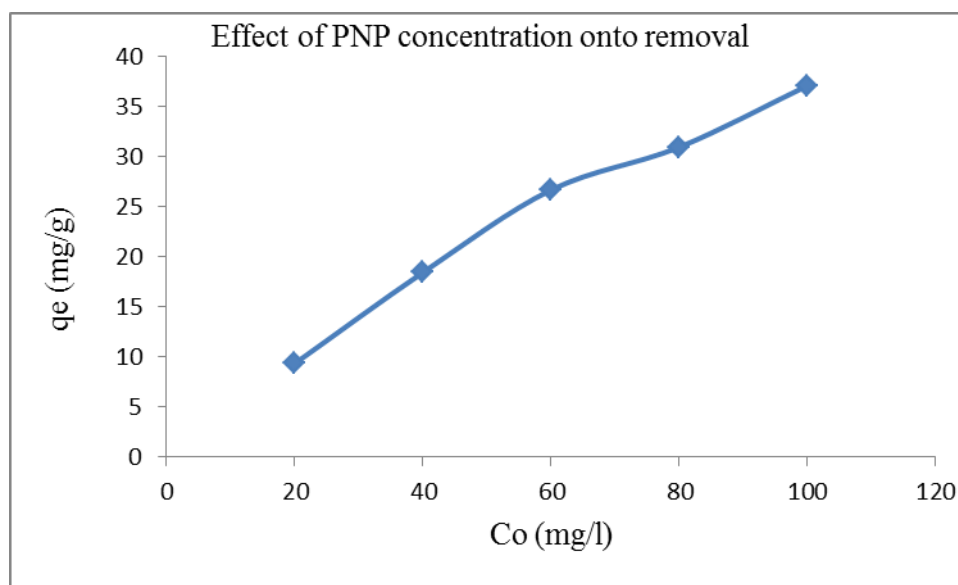
Effect of CFAC		Effect of temperature		Effect of contact time		Effect of pH	
AC wt (mg)	qe (mg/)	Temperature (°C)	qe (mg/g)	Time (minute)	Qe (mg/g)	PH	qe (mg/g)
20	10.57	15	27.79	0	0	2	31.5
50	27.29	25	29.5	1	9.32	4	31.28
100	32.65	35	31	5	24.04	6	30.68
300	36.36	45	31.2	10	27.6	8	20.03
				20	28.68	10	14.01
				60	30.86	12	8.11
				90	31.1		
				120	31.98		
				150	32.43		

The Figure and Table show that the maximum amount of PNP adsorbed was 36.36 mg/g (90.9%) when the amount of CFAC was 0.3g but, the maximum amount of PNP adsorbed at pH 2 although there is no significant adsorption difference between pH 2 and pH from 2 to 6.

Optimum amount of PNP adsorbed 33.43 mg/g (83.5%) was achieved when the temperature was 45 °C. Equilibrium time 150 minute was optimum contact time for the maximum amount of PNP adsorption 32.43 mg/g (80.2%), but most of PNP was adsorbed in first 10 minute.

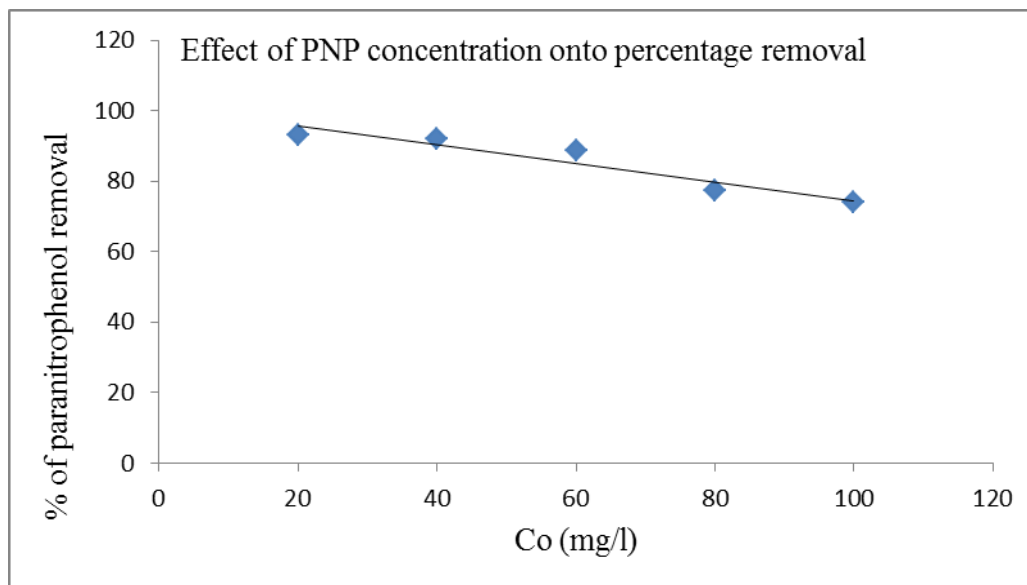
#### 4.8 Effect of PNP concentration

Figure 4.14 shows the effect of initial concentration of PNP on the amount of PNP removal at equilibrium. This figure shows that the adsorbed amount of PNP increases as the PNP concentration increases. Figure 4.15 shows the effect of initial phenol concentration on percentage removal of PNP at equilibrium. This figure shows that increase of concentration decreased the percentage of PNP removal. As phenol concentration increases from 20 mg/L to 100 mg/L, the percentage removal was decreased from 93.2 % to 74.14 %. Dabhade et al.(2009) have showed a similar conclusion that increase of concentration decreased the percentage adsorption when the phenol concentration increases from 50 mg/L to 1000 mg/L, percentage removal was decreased from 56.4 % to 36.3 % [78].



**Figure4.14: Effect of PNP onto the amount removal of PNP by CFAC at (initial pH: 4, temperature: 25°C and solid/liquid ratio 0.1 g/50 mL).**

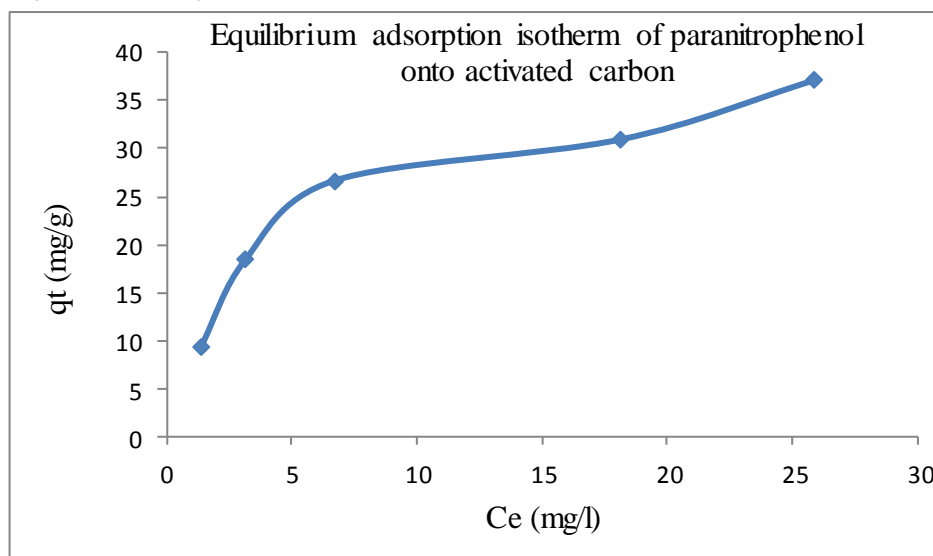




**Figure 4.15:** Effect of PNP onto the percentage removal of PNP by CFAC at (initial pH: 4, temperature: 25°C and solid/liquid ratio 0.1 g/50 mL).

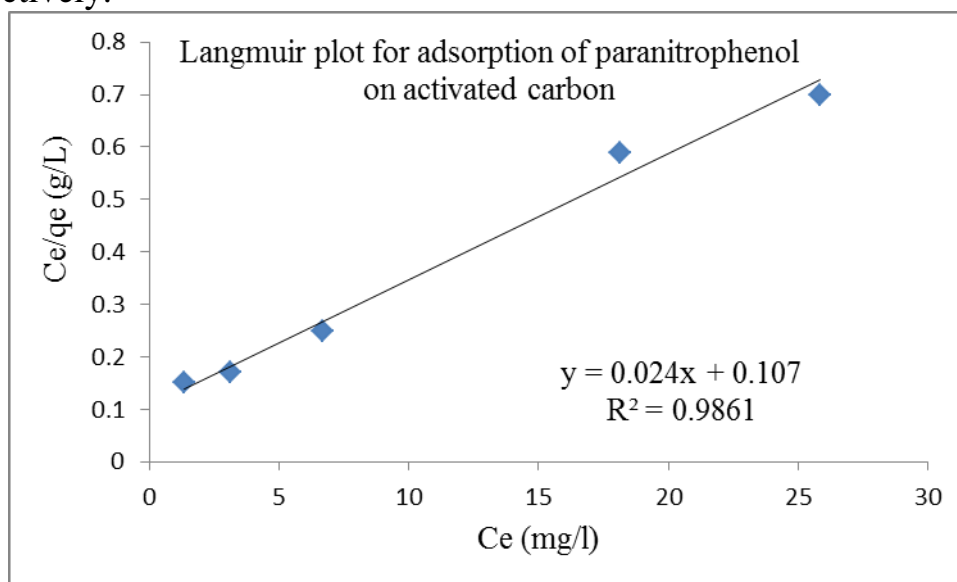
#### 4.9 Adsorption isotherms

In order to design an adsorption system, it is important to study the adsorption isotherms. This is because they give an idea about the adsorption capacity [74]. Adsorption isotherm for PNP onto CFAC at 25°C is given in Figure 4.16.

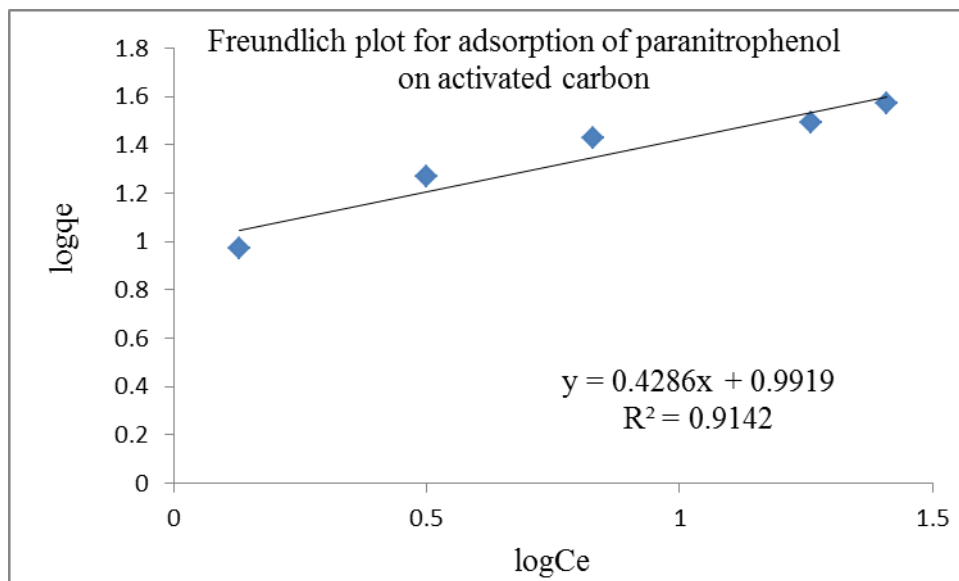


**Figure 4.16: Equilibrium adsorption isotherm of PNP onto CFAC at (temperature: 25 °C, initial pH: 4 and solid/liquid ratio 0.1 g/50 mL).**

In this study, Langmuir and Freundlich isotherm models were used to describe the relationship between the amounts of PNP adsorbed and its equilibrium concentration in solution at 25°C. The fitting of adsorption data to Langmuir and Freundlich isotherm equations was investigated by plotting  $C_e/q_e$  versus  $C_e$  Figure 4.17 and  $\log q_e$  versus  $\log C_e$  Figure 4.18, respectively.



**Figure 4.17: Langmuir plot for PNP adsorption onto CFAC at (Temperature; 25 °C, initial pH: 4 and solid/liquid ratio 0.1 g/50 mL).**



**Figure 4.18:** Freundlich plot for PNP adsorption onto CFAC at (temperature: 25 °C, initial pH: 4 and solid/liquid ratio: 0.1 g/50 mL).

It is clear from table 4.3 the  $R^2$  values that both Langmuir and Freundlich isotherm describe the experimental data, but Langmuir isotherm model describe data better than Freundlich.

On average, a favorable adsorption tends to have Freundlich constant ( $n$ ) between 1 and 10. Larger value of  $n$  (smaller value of  $1/n$ ) implies stronger interaction between the adsorbent and the adsorbate [75]. From Table 4.3 it can be seen that ( $n$ ) value was between 1 and 10 showing favorable adsorption of onto the activated carbon prepared here.

**Table 4.3:** Langmuir and Freundlich isotherm model parameters and correlation coefficient of PNP adsorption on to CFAC.

Isotherm	Langmuir			Freundlich		
Adsorbate	Parameters			Parameters		
	qm (mg/g)	b (L/mg)	$R^2$	KF ((mg/g)(L/mg) <sup>1/n</sup> )	n	$R^2$
PNP	41.67	0.224	0.9861	9.82	2.33	0.9142

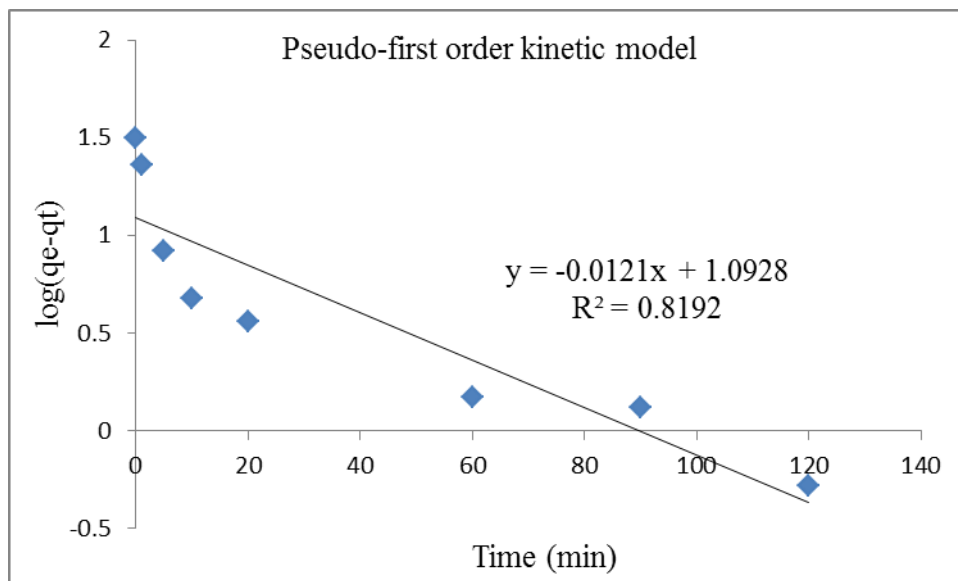
The main properties of Langmuir equation can be expressed in term of separation factor,  $R_L$  defined by McKay et al.(1987) by the following equation:

$$R_L = \frac{1}{(1 + bC_0)} \quad (4.2)$$

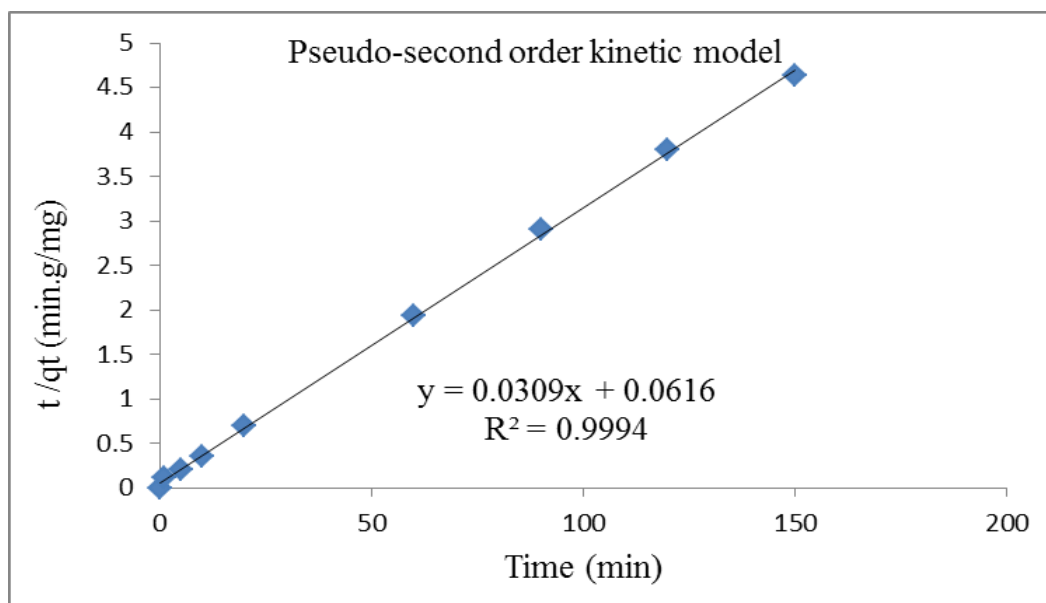
Where  $C_0$  is the initial PNP concentration (mg/L) and  $b$  Langmuir adsorption constant. The  $R_L$  show the adsorption to be un favorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), irreversible ( $R_L = 0$ ) [76]. The value of  $R_L$  for CFAC was founded to be 0.053, which show that the adsorption system was favorable.

#### **4.10 Kinetics of PNP Adsorption**

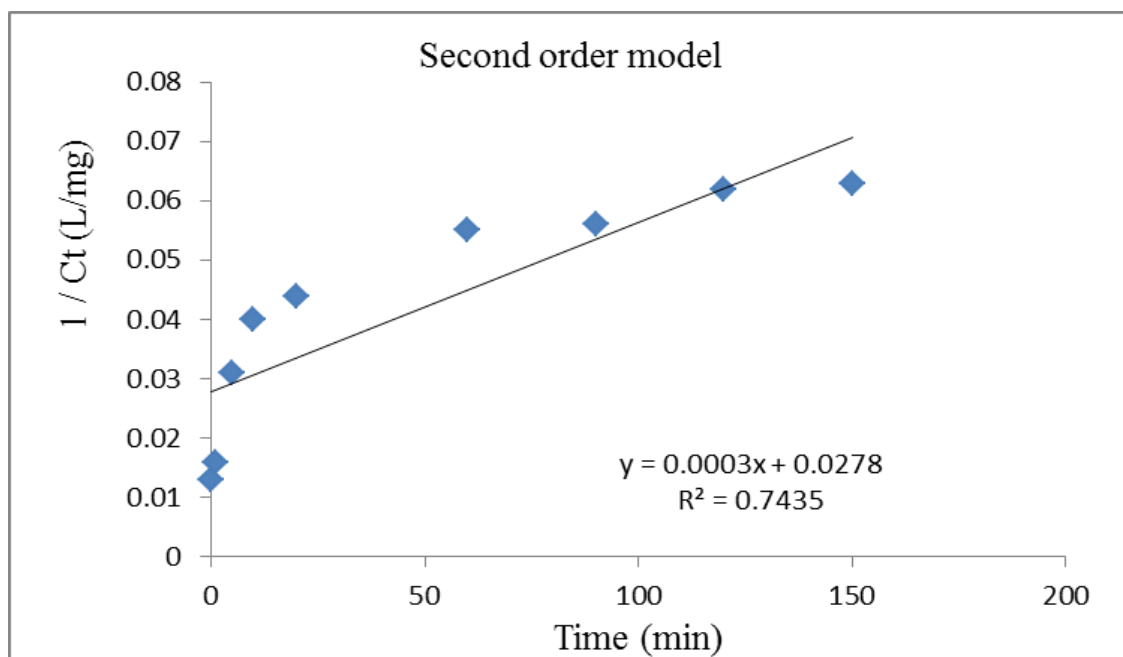
In order to investigate the mechanism of PNP adsorption process on CFAC, the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, second order kinetic model and the intra-particle diffusion model were all used to test the experimental data. The results are shown in Figures 4.19, 4.20, 4.21 and 4.22, respectively.



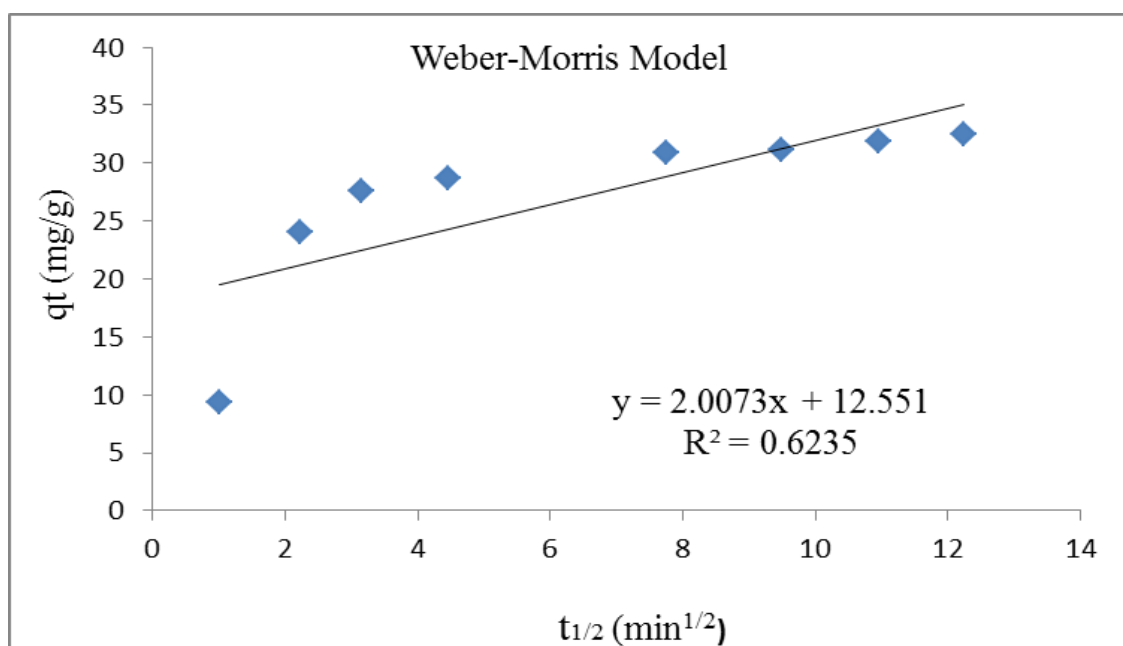
**Figure 4.19: Kinetics of PNP removal according to the pseudo-first-order model by CFAC at (initial conc: 80 mg/L, initial pH: 4, temperature: 25 C° and solid/liquid ratio 0.1 g/50 mL).**



**Figure 4.20: Kinetics of PNP removal according to the pseudo-second-order model by AC at (initial conc: 80 mg/L, initial pH: 4, temperature: 25 °C and solid/liquid ratio 0.1 g/50 mL)**



**Figure 4.21: Kinetics of PNP removal according to the second-order model by CFAC at (initial conc: 80 mg/L, initial pH: 4, temperature: 25 °C and solid/liquid ratio 0.1 g/50 mL).**



**Figure 4.22: Kinetics of PNP removal according to the intra-particle diffusion model (Weber-Morris model) by CFAC at (initial conc: 80 mg/L, initial pH: 4, temperature: 25 °C and solid/liquid ratio 0.1 g/50 mL).**

The correlation coefficients and other parameters calculated for the Pseudo-first-order model and pseudo-second-order model are listed in Table 4.4 and second order model listed in Table 4.5. From Table 4.4 and Table 4.5, it is clear that the correlation coefficient values ( $R^2$ ) of the pseudo-second-order model for adsorbents greater than those obtained for the pseudo-first-order model and second order model. On the other hand,  $q_e$  (exp) values for the first-order-rate expression and  $C_0$  for second order model do not agree with the calculated ones obtained from the linear plots. In contrast,  $q_e$  (calc) values for the second-order-model are close to  $q_e$  (exp) for both adsorbents. Thus, higher correlation coefficients of pseudo-second-order equation and the  $q_e$  (calc) values close to the experimental ones indicates that the pseudo-second-order kinetic model might be more suitable to describe the kinetic of adsorption processes of PNP onto adsorbents. This suggests that during the adsorption of PNP, there was chemisorption between the adsorbent surface and adsorbate [77-78].

**Table 4.4: Pseudo-first-order and pseudo-second-order kinetic model parameters for PNP adsorption onto CFAC at 25°C.**

Adsorbent	$q_e$ (exp) (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		$k_1$ (min <sup>-1</sup> )	$q_e$ (calc) (mg/g)	$R^2$	$k_2$ (g/mg min)	$q_e$ (calc) (mg/g)	$R^2$
CFAC	32.43	0.0279	12.38	0.8192	0.0155	32.36	0.9994

**Table 4.5: Second-order kinetic model parameters for PNP adsorption onto CFAC at 25 °C.**

Adsorbent	$C_0$ (exp) (mg/L)	second-order kinetic model		
		$K_2^*$ (g/mg.min)	$C_0$ (calc) (mg/L)	$R^2$
CFAC	80	0.0003	35.7	0.7435

The Table 4.6 show that the values of  $k_2q_e$  in this work are higher than the value obtained in other work because PNP adsorption more favorable than phenol due to the withdrawing group  $-\text{NO}_2$  and good properties of CFAC to adsorption. Therefore, electron-withdrawing favors the formation of electron donor-acceptors complex between PNP and surface of CFAC [2].

**Table 4.6: Pseudo-second order parameters for phenol and PNP adsorption onto various adsorbents**

Activated carbon	Adsorbate	$k_2$ g/(mg.min)	$R_2$	$k_2q_e$ ( $\text{min}^{-1}$ )	Reference
Pumkin stem	phenol	1.63	0.987	0.0494	(Ekpete, 2011)
Pistachio shell	phenol	0.97	1.000	0.2159	(Tseng <i>et al.</i> , 2010)
CFAC	PNP	0.0155	0.9994	0.502	This work

The values of the intra-particle diffusion constants and the correlation coefficients obtained from the linear plots of  $q_t$  versus  $t^{1/2}$ , given in Figure 4.22, are summarized in Table 4.7. Figure 4.22 implies that the rate of PNP adsorption onto CFAC is limited by mass transfer across the boundary layer due to the follwoin reasons:



1. linear line not pass through origin point.
2. positive intercept value.
3. low value of correlation coefficient.

**Table 4.7: Intra-particle diffusion kinetic model parameters for PNP adsorption onto CFAC at 25 °C.**

<b>Adsorbent</b>	<b><math>k_b</math> (mg/g min<sup>1/2</sup>)</b>	<b><math>R^2</math></b>	<b>A(mg/g)</b>
<b>CFAC</b>	2.0073	0.6235	12.551

## Conclusion:

1. Activated carbon produced from cypress fruits give a good percentage of yield reaching 51.8% .
2. Optimum percent of PNP removal 90.9 % when adsorbent dosage 0.3g and PNP concentration 80mg\L.
3. Percentage removal of PNP increases when the concentration of PNP decreases with maximum percentage removal reaching 93.2% when PNP concentration was 20mg\L and 0.1g CFAC.
4. At lowering pH from 6 to 2 the PNP adsorbent increases slightly, but the decrease of adsorbent at pH from 6 to 12 is highly extreme.
5. The results showed that equilibrium time for PNP adsorption is 150min, but most the adsorption attained within the first ten minute.
6. PNP adsorption uptake slightly increases when temperature is increased.
7. The pseudo-first-order model and second order model correlation coefficient values ( $R^2$ ) are low that fail to describe the experimental results.
8. The results showed that PNP adsorptions onto CFAC can be described by pseudo-second-order model.
9. Both Frenundlich and Langmuir equilibrium model describe the adsorption of PNP, but Langmuir model describe very well the adsorption.

10. The separation factor for Langmuir equation ( $R_L$ ) for CFAC was found to be 0.053, which shows that the adsorption system was favorable.
11. The values of the intra-particle diffusion constants and the correlation coefficients imply that the rate of PNP adsorption onto CFAC is limited by mass transfer across the boundary layer.

**Suggestions for future work**

Although this research studies many properties of CFAC, factors affecting the adsorption of PNP, and many models of adsorption, there are many areas need further investigation. These include:

1. Studying porosity of CFAC.
2. More investigation of the effect of particle size on adsorption.
3. Study the effect of change chemical activating agent and physical activation on the properties of AC produced.
4. More study the effect of PH on adsorption efficiency especially when the medium become base by comparing the absorbance with or without CFAC using suitable standard to accommodate the change that happen when added base solution onto phenol compounds.
5. Study total phenol adsorption onto CFAC.
6. Investigate adsorption thermodynamic.
7. Study economic efficiency of using CFAC on treatment of waste water .

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كلية الدراسات العليا

معالجة المركبات الفينولية الملوثة في المياه العادمة باستخدام الكربون  
المنشط المحضر من ثمار السرو

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إشراف

د.شحدة جودة

د.أحمد أبو عبيد

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### الملخص

إن هذا العمل يركز على تحضير كربون منشط من ثمار السرو بطريقة كيميائية باستخدام حمض الفوسفوريك ( $H_3PO_4$ ) كمادة منشطة ومن ثم دراسة خصائص هذا الكربون المنشط وقدرته على ادمصاص مركب البارانيتروفينول حيث ان المركبات الفينولية تنتج بكميات كبيرة من عدة مصادر ويتم التخلص منها بدون معالجة في شبكات الصرف الصحي أو الوديان الأمر الذي يؤدي إلى تلوث مصادر المياه.

تم استخدام فرنًا حراريًا على درجة حرارة 700 مئوي من أجل انتاج كربون نشط كيميائيًا من ثمار شجرة السرو، بنسبة انتاج عالية تصل إلى (51,8%)، و لإيجاد المساحة السطحية تم استخدام طريقة الرقم اليودي وقد تبين أن المساحة السطحية تساوي (524,1م<sup>2</sup>/غم)، مع العلم انه تم التحقق من خصائص الادمصاص للبارانيتروفينول بواسطة الكربون المحضر من ثمار السرو عن طريقة دراسة اثر كمية الكربون، تركيز البارانيتروفينول، درجة الحموضة، درجة الحرارة، و زمن التماس.

وقد أشارت النتائج أشارت إلى أن أفضل نسبة استخلاص للبارانيتروفينول كانت(90,9%) عندما كانت كمية الكربون المحضر المستخدمة ( 0.3غم) وتركيز البارانيتروفينول(80ملغم/لتر).

أما فيما يتعلق بتأثر تركيز البارانيتروفينول فكانت أفضل نسبة استخلاص له ( 93.2 % ) عندما كان تركيز البارانيتروفينول ( 20ملغم/لتر)، و كتلة الكربون المحضر المستخدمة ( 0.1غم). وفيما يخص درجة الحموضة، فقد توصلت الدراسة إلى أنه كلما انخفضت قيمة درجة الحموضة من 6



## ج

الى 2 تزداد عملية الادمصاص بشكل طفيف، ولكن عند الانتقال من درجة حموضة 6 الى 12 تقل عملية الادمصاص بشكل كبير و واضح جدا. أما فيما يتعلق بأثر درجة الحرارة على نسبة استخلاص البارانيتروفينول وجدت الدراسة أن درج الحرارة تزيد من نسبة الاستخلاص بشكل بسيط. ولقد وجدت الدراسة إلى أن زمن الاتزان لعملية الادمصاص هو 150 دقيقة ولكن معظم هذه العملية تمت في الدقائق العشرة الأولى من هذه العملية.

تم دراسة عملية الادمصاص عند الاتزان وقد وجد أن معادلتى (لانجموير) و (فرنديلش) تفسران النتائج بشكل جيد، لكن معادلة (لانجموير) تفسر النتائج بشكل أفضل. وقد وجد أن معامل الفصل لمعادلة (لانجموير) يساوي (0.053) وهذا يدل على أن عملية الادمصاص مرغوبة. ومن أجل التحقق من عملية الادمصاص، تم تطبيق أربعة نماذج مبسطة للحركة، وهي: نموذج الاعتماد من الدرجة الأولى ظاهريا، ونموذج الاعتماد من الدرجة الثانية ظاهريا، ونموذج الاعتماد من الدرجة الثانية، ونموذج تدفق الدقائق إلى داخل الجسيمات. وقد اتفقت النتائج التي تم الحصول عليها من ادمصاص البارانيتروفينول مع الكربون المحضر مع نموذج الاعتماد من الدرجة الثانية ظاهريا حيث كانت قيم المعاملان  $(R^2)$  و  $k_2q_e$  هي: (0.9994) و (0.502) على التوالي.

وقد وجدت الدراسة من خلال ثابت الانتشار الخارجي للجزيئات ومعامل الارتباط  $(R^2)$  ان عملية انتقال الكتل بين الطبقات محدودة وان عملية الادمصاص تتم على حدود الطبقات وعلى السطح الخارجي.

وفي الختام ، نسأل الله تعالى التوفيق والسداد في الدارين، والحمد لله رب العالمين.