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Nitrate removal from water using activated carbon prepared from olive stone by microwave heating

M.Sc. Thesis By

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أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

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Nitrate removal from water using activated carbon prepared from olive stone by microwave heating

ازالة النترات من الماء باستخدام الكربون المنشط المحضر من نوى الزيتون بواسطة تسخين الميكرويف

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II

Abstract

Nitrate is one of the common contaminants of water resources around the world. The main reasons for nitrate increase are human activities such as excessive use of pesticides, synthetic nitrogen fertilizer and animal manure in agriculture.

The investigation of removing efficiency of nitrate from synthetic water by using the olive stones activated carbon (OSAC) prepared by microwave heating was the major objective of this study.

Through the current research, the olive stones (OS) have been carbonized at 700 ^{o}C at inert environment by flowing nitrogen (N_2) (300-500 cm^3/min) for one hour and then been activated by microwave radiation at several activation times (5, 10, 20, 30 and 40 min) with assistant of zinc chloride ($ZnCl_2$) chemical reagent with impregnation ratio (IR) of 1.6:1 w/w, the highest achieved surface area of prepared activated carbon (PAC) was 709.5 m^2/g at time of activation 30 min.

Effect of reaction parameters (i.e., pH, adsorbent dosage, contact time, initial concentration of adsorbate and temperature) on the nitrate removal efficiency was observed by batch equilibrium study. The results indicated that maximum adsorption capacity of 5.76 mg/g of prepared OSAC was achieved at 90 min equilibrium time, pH 4, 2 g adsorbent dosage and 80 mg/L initial concentration of nitrate. Meanwhile, the temperature slightly affected the effectiveness of AC adsorption. This indicates that AC can be used in treatment under various temperatures without affecting the adsorbent efficiency.

The equilibrium adsorption data were interpreted using Langmuir and Freundlich models. The adsorption of nitrate on OSAC was better represented by the Langmuir model. Three simplified kinetic models were tested to investigate the adsorption mechanism and potential rate-controlling. pseudo-second order model results show the best fit of the kinetic data. Therefore, it is safe to infer that nitrate adsorption systems on OSAC followed pseudo-second order kinetic model.

According to this research, OSAC prepared by microwave can be used for the efficient removal of nitrate from contaminated water.

ملخص الدراسة

تعتبر النترات واحدة من الملوثات الشائعة في مصادر المياه حول العالم. يعتبر السبب الرئيسي لزيادة النترات هو الأنشطة البشرية مثل الاستخدام المفرط لمبيدات الآفات والأسمدة النيتروجينية الاصطناعية وروث الحيوانات في الزراعة.

يعتبر التحقق من كفاءة إزالة النترات من الماء الاصطناعي باستخدام الكربون المنشط المحضر من أحجار الزيتون بواسطة حرارة الميكرويف هو الهدف الرئيسي لهذه الدراسة.

من خلال هذا البحث تم تفحيم أحجار الزيتون عند 700 درجة مئوية في بيئة خاملة عن طريق تدفق النيتروجين (300−500سم3 / دقيقة) لمدة ساعة واحدة ثم تم تنشيطها باستخدام إشعاع الميكروويف عند أزمان مختلفة للتنشيط وهي (5 −10 −20 −30 −40 دقيقة) مع مساعدة العامل الكيميائي كلوريد الخرصين $ZnCl_2$ بنسبة 1.6:1، كانت أعلى مساحة سطحية للكربون المنتج 709.5 متر2/ جم عند وقت التنشيط 30 دقيقة.

تم تحديد تأثيرات عوامل التفاعل المختلفة (على سبيل المثال، درجة الحموضة، وقت الاتصال، الجرعة، التركيز الأولي للممتز ودرجة الحرارة) على كفاءة إزالة النترات. أشارت النتائج إلى أن سعة الادمصاص القصوى هي 5.76 ملغم / غرام من OSAC المحضر قد تم تحقيقه في وقت توازن قدره 90 دقيقة، درجة حموضة 4، 2 غرام من الجرعة الممتزة و تركيز النترات الأولي بنسبة 80 مجم / لتر. وفي الوقت نفسه ، أثرت درجة الحرارة بشكل طفيف على فعالية ادمصاص الكربون المنشط. هذا يشير إلى أنه يمكن استخدام الكربون المنشط في المعالجة تحت درجات حرارة مختلفة بدون التأثير على كفاءة الادمصاص.

تم تفسير بيانات توازن الادمصاص باستخدام نماذج لانجومير وفريندلك. تم تمثيل ادمصاص النترات على الكربون المنشط بشكل أفضل من خلال نموذج لانجومير. تم اختبار ثلاثة نماذج حركية مبسطة للتحقيق في آلية الادمصاص والتحكم في المعدل المحتمل. أظهرت نتائج نموذج الترتيب الثنائي (pseudo−second−order) ملائمة أفضل للبيانات الحركية. لذلك، من الأمن الاستدلال على أن أنظمة ادمصاص النترات على الكربون المنشط المحضر من نوى الزيتون تتبع النموذج الحركي من الدرجة الثانية.

وفقا لهذا البحث ، يمكن استخدام الكربون المنشط المحضر من نوى الزيتون بواسطة تسخين الميكرويف في الإزالة الفعالة للنترات من المياه الملوثة

Epigraph Page

بسم الله الرحمن الرحيم

Olive was mentioned in Quran 7 times:

قال تعالى: (وَجَنَّاتٍ مِّنْ أَعْنَابٍ وَالزَّيْتُونَ وَالرُّمَّانَ) الأنعام 99

قال تعالى: (وَالزَّيْتُونَ وَالرُّمَّانَ مُتَشَابِهًا وَغَيْرَ مُتَشَابِهٍ كُلُواْ مِن ثَمَرِهِ إِذَا أَثْمَرَ) الأنعام 141

قال تعالى: (يُنبِتُ لَكُم بِهِ الزَّرْعَ وَالزَّيْتُونَ وَالنَّخِيلَ وَالأَعْنَابَ) النحل 11

قال تعالى: (وَشَجَرَةً تَخْرُجُ مِنْ طُورِ سَيْنَاءَ تَنْبُتُ بِالدُّهْنِ وَصِبْغٍ لِّلْآكِلِينَ) المؤمنون 20

قال تعالى: (يُوقَدُ مِن شَجَرَةٍ مُّبَارَكَةٍ زَيْتُونِةٍ لَّا شَرْقِيَّةٍ وَلَا غَرْبِيَّةٍ) النور 57

قال تعالى: (وَزَيْتُونًا وَنَخْلًا) عبس 24

قال تعالى: (وَالتِّينِ وَالزَّيْتُونِ) التين 1

And in Sonah:

قال رسول الله صلى الله عليه وسلم: (كلوا الزيت وأدهنوا به فإنه يخرج من شجرة مباركة)

Dedication

I would like to dedicate this thesis to everyone who sacrificed his life for the others to ensure better life and prosperous future for humankind. In addition, I dedicate it to my beloved parents, precious wife, great brothers, sisters, lovely son (Jamal), and all my friends who supported me through my difficult times.

Abdallah

Acknowledgment

First and foremost, I would like to praise Allah the almighty for the patience and assistance He granted me to accomplish this thesis.

I would like to express my greatest gratitude to my supervisors, Dr. Khalil Alastal and Dr. Tamer Alslaibi for their invaluable guidance, supervision and advice throughout this study. The attainment of this level of success would not have been possible without them.

Special thanks to Middle East Desalination Research Center (MEDRC) and the Palestinian Water Authority (PWA). I am very grateful to all of them for funding and covering most of the research's costs

I am grateful to the academics, administrative staff and my colleagues in the Civil Engineering department of the Islamic University for their support and assistance during my master journey.

Many thanks go to all my friends and colleagues in Islamic Relief Association- Palestine office (IRPAL) for their support, encouragement and for great environment that helped me in completing this research.

Special thanks are directed to my lovely parents, wife, son, brothers and sisters for their understanding, patience and encouragement.

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List of Abbreviations

Abbreviation	Name
AC	Activated Carbon
OSAC	Olive stones activated carbon
CAC	Commercial activated carbon
PAC	Prepared activated carbon
NO_3^-	Nitrate
BET	Brunauer- Emmett-Teller
IR	Chemical impregnation ratio
R^2	Coefficient of determination
RL	Dimensionless equilibrium parameter
pH	Potential Hydrogen
SA	Surface area
°C	Celsius
cm^3/min	Cubic centimeter per min
g	Grams
m^3	Cubic meter
mg/L	Milligram per Liter
ml	Milliliter
mm	Millimeter
$ZnCl_2$	Zinc chloride

SEM	Scanning Electronic Microscope
IUPAC	International Union of Pure and Applied Chemistry
CMWU	Coastal Municipalities Water Utility
PWA	Palestinian Water Authority
WHO	World Health Organization
EPA	Environmental Protection Agency
PCBS	Palestinian Central Bureau of Statistics

Chapter 1

Introduction

Chapter 1

Introduction

1.1. Background and context

Nitrate is one of the common contaminants of water; whether it is groundwater, surface water, or other water resources around the world. The main causes for nitrate increase are human activities, such as: excessive use of pesticides, synthetic nitrogen fertilizers, and animal manure in agriculture. It exhibits serious risks to human health (Majumdar & Gupta, 2000) (W. Gao et al., 2018). Increased concentration of nitrate in drinking water leads to two adverse health effects. It causes induction of "methemoglobinemia", especially in infants. Furthermore, some studies have shown that an increase in the concentration of nitrate ions in drinking water may also be responsible for causing various types of cancer in humans (Bhatnagar & Sillanpää, 2011). For the purpose of risk mitigation, world health organization (WHO) recommend a maximum nitrate concentration in drinking water not to exceed 50 mg/l (WHO, 2017), while the Water Palestinian Standards WPS recommends a maximum nitrate concentration in drinking water not to exceed 70 mg/l (PWA, 2016).

Nitrate ions are considered to be highly soluble in water, so they have a low tendency to be removed by traditional water treatment methods such as filtration. Various techniques and methods have been applied to remove nitrates from water resources, by biological removal (Mook et al., 2012; Park & Yoo, 2009) , reverse osmosis (Ali & Abdel-Hameed, 2018), ion exchange (Bergquist, Bertoch, Gildert, Strathmann, & Werth, 2017; Green & Tarre, 2018), electro dialysis (Belkada et al., 2018; Bi, Peng, Xu, & Ahmed, 2011), chemical denitrification, chemical reduction (Mirabi, Ghaderi, & Sadabad, 2017) and adsorption (Hamoudi & Belkacemi, 2013; Katal, Baei, Rahmati, & Esfandian, 2012).

Activated carbon (AC) is widely used as adsorbent in adsorption processes, due to their large surface area, high porosity, high surface reactivity, mesoporous structure and high adsorption capacity (Turan et al., 2013)

The annual production of Activated Carbon (AC) in worldwide is approximately 520,000 tons, 400,000 tons of which is used in water and air treatment (Chien, Huang, Wang, Chao, & Wei, 2011). AC can be produced from any carbon-rich materials such as coal, biomass and lignite. Recently, there is a growing interest in the production of AC from secondary agricultural products (agricultural by-products), which are produced annually in large quantities. AC producing from agricultural waste can enhance the economic return and decrease pollution (Martinez, Torres, Guzman, & Maestri, 2006). Agricultural by products are rich in carbon such as husks, fruit seeds, grains, rice, fruit harvest, olive stone, oak, pecan, walnut husk, and stone-core fruits (Martinez et al., 2006).

Olive is one of the most fruit growing crops in the world. Olive cultivation plays an important role in its rural economy, local heritage and environmental protection. The Middle East regions and Mediterranean counties are the largest producer of olive, providing 98% of the total cultivated area and 99% of the total olive oil production (Yakout & El-Deen, 2016) . The world production of olive oil reached 2.854 million tons for the current crop year (Sep.2017 – Aug. 2018). 15 million tons of olive stone (OS) were produced through annual olive oil production (the International Olive Council, 2011). OS are cheap, quite abundant and rich in carbon, so it is preferred to be used for AC manufacturing and in water and wastewater treatment (Alslaibi, Abustan, Ahmad, & Foul, 2014a). Also, olive stones can be used as a source of energy (the International Olive Council, 2011).

1.2. Problem statement

Water pollution is one of the important issues with several consequences on life on earth (Khatri, Tyagi, & Rawtani, 2016). This is generally the situation in Mediterranean region, especially in the Gaza strip. Recently, there is an increase in the availability of inorganic nitrate over the world, especially in aquatic systems. Nitrate is a widespread pollutant because it is highly soluble in water (Thompson, 2001)

In Gaza strip, nitrate concentrations exceeds the acceptable limit (as recommended by WHO and WPS) in various water sources. This is considered as a major environmental

concern through various human activities such as agricultural, industrial, pesticide use, improper treatment of industrial waste, urban runoff, sewer leakage, waste leaching in groundwater and sewage effluents (Gu, Ge, Chang, Luo, & Chang, 2013; Khatri & Tyagi, 2015; PWA, 2016). It is known that nitrate pollutant is a threat to people health and cause many health problems such as hemoglobinuria (Fewtrell, 2004), diabetes and cancer (Bryan & Loscalzo, 2011) (Bhatnagar & Sillanpää, 2011). Removal of nitrates from aquatic environments such as surface water bodies and groundwater is important to avoid the health problems. Several techniques have been applied such as ion exchange, electrochemical methods, reverse osmosis, biological methods and adsorption. However, most of these techniques have several limitations. Therefore, an efficient and cost-effective method is needed to treat water contaminated with nitrates. Adsorption was found to be fast, effective, inexpensive, attractive and widely applicable technique compared to other methods because of their efficiency, comfort, ease of operation, design simplicity, economic and environmental reasons (Gupta, Gupta, Rastogi, Agarwal, & Nayak, 2011). As a result, much work has been carried out on adsorption to treat water and wastewater. Activated carbon (AC) is widely used for adsorption processes, due to their large surface area, high porosity, high surface reactivity, mesoporous structure and high adsorption capacity (Turan et al., 2013). However, the use of commercial AC is still limited because of using natural and non-renewable materials such as coal or wood, and therefore, are still considered relatively expensive. In recent years, as a result of lower costs, there has been a strong tendency towards the use of agricultural by-products and waste materials for production of AC (Arena, Lee, & Clift, 2016). These include rice husks (D. Liu et al., 2016), date pits (Awwad, El-Zahhar, Fouda, & Ibrahium, 2013), bamboo husk (Asberry, Kuo, Gung, Conte, & Suen, 2014), durian peel (Kamaruddin, Yusoff, & Ahmad, 2012), olive waste (Hjaila, Baccar, Sarrà, Gasol, & Blánquez, 2013),chestnut shell (Ertaş & Öztürk, 2013), palm shells (Lim, Srinivasakannan, & Al Shoaibi, 2015), coconut coir pith (Shukla & Shukla, 2013).

Previously, conventional heating method is usually used to prepare activated carbon. This method requires a long time to reactivate and consume more energy because it warms up

the surface of the particle and then gradient to its interior. Recently, researchers have tended to study the preparation of activated carbon (AC) using microwave heating technology. During microwave heating, the massive thermal gradient from the inside of the particle turns to the surface. These allow the microwave-induced interaction to proceed more quickly and effectively, resulting in saving the energy and short activation time (K. Yang et al., 2010).

However, some of previous studies have addressed the use of AC from OS by using microwave heating. Also, a few studies have examined the efficiency of removing nitrates by AC produced from OS.

In this research, we will carry out a set of experiments using batch equilibrium study to verify the possibility and efficiency of removing nitrates from water using OSAC prepared by the microwave through chemical activation method.

1.3. Scope of the study

Data and statistics about the nitrate concentrations in water in the Gaza Strip were collected from reports and studies issued by the authorities responsible for water services such as Coastal Municipalities Water Utility (CMWU) and the Palestinian Water Authority (PWA).

Olive crushed stones were collected from local olive mills and treated and dried. It was then burned to a high temperature in an inert atmosphere using N_2 gas (carbonization). After that, the char was activated using the heat generated by the microwave device with the help of the $ZnCl_2$ activation factor in an inert atmosphere using N_2 gas. The activation was performed applying different heating times (5,10,20,30 and 40 min). This was conducting for the purpose of choosing the best time for char activation. Experiments were carried out to detect some properties of AC such as surface area, ash content and bulk density.

Laboratory tests were conducted to verify the efficiency of removing nitrates from water by the prepared activated carbon throw batch equilibrium study. The tests were

synthetically performed using synthetic water samples of different concentrations of nitrate, dosage, pH, contact time and temperature.

Equilibrium data were studied using Langmuir and Freundlich isotherm models. Adsorption kinetics were fitted to pseudo-first order, pseudo second order, and intra-particle diffusion models.

1.4. Study limitation

- Removal of nitrates from water was examined only by the batch equilibrium study.
- Synthetic water samples were used in experiments to test the efficiency of nitrate removal using activated carbon rather than using real water samples.
- The acetic acid method was used to determine the surface area of the activated carbon instead of the BET method because it is not available in the Gaza Strip.
- Fourier Transform Infrared (FT-IR) spectroscopy (used to determine chemical characteristics of surface functional group of char/ACs) was not carried out because it is not available in the Gaza Strip.

1.5. Objectives

The objectives of this study are as follows:

- to evaluate and compare removal efficiency of nitrate from synthetic water using commercial activated carbon and prepared activated carbon.
- to determine adsorption capacity of activated carbon for nitrate using best fit isotherm model and to determine adsorption kinetics.
- to manufacture activated carbon from olive stones by using microwave technique at different activation times and specific radiation power and impregnation ratio.
- to determine the optimum operational conditions (pH, contact time, dosage, initial concentration and Temperature) of nitrate removal by activated carbon.

1.6. Structure of thesis

This research is presented in five chapters as follows:

Chapter 1: Introduction

Provide background on research topic, presents problem statement that provide some basic and rationale to identify research directions to be followed in this research. Next, the objectives, scope and layout of thesis are presented.

Chapter 2: Literature review

This chapter includes a comprehensive reviews of literature pertaining to water contamination with nitrate, source of nitrate in environment, health effects and nitrate treatment techniques. Adsorption process, definitions, factors influencing adsorption, and adsorption isotherm and kinetics. AC definition, production methods, precursors, factors affecting preparation and application in nitrate removal.

Chapter 3: Research methodology

This chapter presents equipment, tools, methods, chemicals and tests used. Procedures of AC production, operational parameter, characterization of activated carbon, experimental work and batch adsorption studies are explained

Chapter 4: Results and discussions

Provides characteristics of char and produced activated carbon, effect of factors (dosage, pH, contact time, temperature and initial concentration) on removing nitrate, determine the optimum removal efficiency of nitrate and presents Freundlich and Langmuir isotherms. Also, determine adsorption kinetics results.

Chapter 5: Conclusions and recommendations

Presents the main findings and conclusions of the study. Additionally, and based on the understanding of the research results, several recommendations are presented for related upcoming works in these field.

Chapter 2

Literature review

Chapter 2
Literature review

2.1. Introduction

This chapter consists of four sections. The first section discusses the risks of water pollution in nitrates, their sources and the techniques used to remove them. Second section presents the characteristics of the adsorption process, its types and the factors affecting it. Third Section shows the mechanism of activated carbon production and the factors affecting it. Section four shows the advantages of the use of olive stone, its uses and olive mills located in the Gaza Strip.

2.2. Nitrate

2.2.1. Nitrate sources and chemistry

Nitrate contamination in different aquatic sources as surface and ground water become an increasingly important problem in many countries around the world (Khatri et al., 2016). Nitrate is a widespread pollutant because it is highly soluble in water (Thompson, 2001). The main cause of increased nitrate water pollution is human activities. The main source of nitrate water pollution is the use of agricultural nitrogen fertilizers (W. Gao et al., 2018). Other common sources of nitrate contamination include wastewater irrigation, industrial processes, sewage tanks, urban runoff, animal manure, chemical pesticides and domestic wastes effluents (Gu et al., 2013; Khatri & Tyagi, 2015).

2.2.2. Health effects of Nitrate

Nitrates, due to its high solubility, it is a widespread pollutant and poses a threat to human health. High concentrations of nitrate can potentially cause several health problem such as blue-baby syndrome or methemoglobinaemia in infants, blood in stool and urine, abdominal pain, weakness, mental depression, vomiting, diabetes, diarrhea, hypertension, hanges in the immune system, increased infant mortality, spontaneous abortions and respiratory tract infections (Batheja, Sinha, & Seth, 2009). Some studies have shown that

an increase in the concentration of nitrates in drinking water may also be responsible for causing various types of cancers in humans (Bhatnagar & Sillanpää, 2011).

For these reasons, it is very important to decrease the nitrates from the water for acceptable range. To reduce the risk to human health due to nitrates, WHO has put a maximum limit of nitrate concentration to no more than 50 part per million (ppm) (WHO, 2017).

2.2.3. Nitrate in Gaza strip

Water in the Gaza Strip is mainly obtained from the coastal aquifer, which has been breached by the Mediterranean Sea, leading to increased salinity in groundwater. The extraction of coastal aquifers in 2016 was estimated at 200 million m^3/year, but the annual sustainable yield of the aquifer within the Gaza Strip is estimated at 55 million m^3/year (PWA, 2016).

Like all countries in the world, water pollution is one of the most common problems in the Gaza Strip. Nitrate is the most common contaminants of which. Anthropogenic activities are the main reason for the increased concentration of nitrates to the harmful level of water in the Gaza Strip. Sewage tanks, industrial wastes, and human sewage are among the main causes of nitrate water pollution. Another major source is nitrogenous fertilizers, where Gaza farmers still consider nitrogen fertilizers to be the cheapest and best-growing fertilizers. Also, the use of animal and poultry manure as natural fertilizers on land in agriculture may be considered as another potential source of nitrate leaching to the ground water (Al-Absi, 2008). As shown in the nitrate contour map for 2016 in Figure (2.1), it is clear that the concentration of nitrate in groundwater supplied in municipal wells ranges from 40 to more than 300 mg/L. 14.1% of these wells have nitrate concentration less than 50 mg/L (WHO limit), while the remaining 85.9% exceeded the level of nitrate allowed by the WHO (2017). 75% of municipal wells have nitrate concentration more than the acceptable limit in water Palestinian standards that 70mg/l.
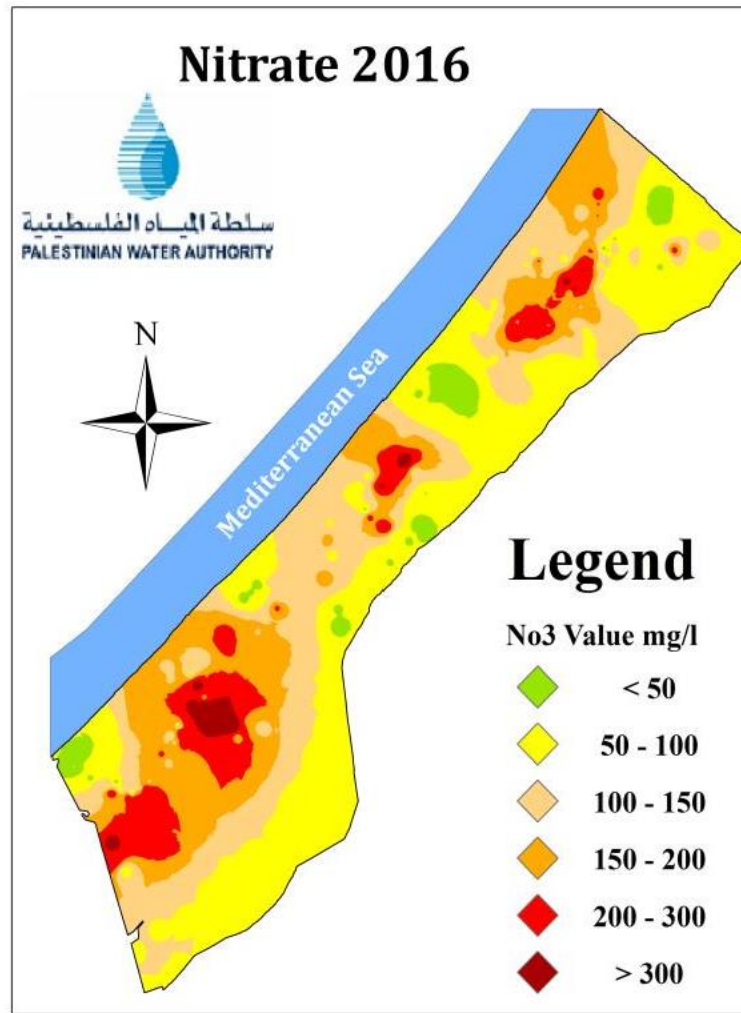
Figure (2.1): Nitrate contour map in the Gaza Strip, Palestine, 2016 (PWA, 2016)

2.2.4. Nitrate treatment techniques

Nitrate treatment techniques were categorized into five major types: reverse osmosis (Ali & Abdel-Hameed, 2018), ion exchange (Bergquist et al., 2017), and electrodialysis (Bi et al., 2011) which remove nitrate to a concentrated waste stream. while biological denitrification (Mook et al., 2012; Park & Yoo, 2009) and chemical denitrification (Mirabi et al., 2017) transform nitrate to other nitrogen species through reduction (Davis, 2012).

The choice of the most appropriate treatment option depends on the key factors identified for the needs and priorities of individual water systems. A short list of the basic design

considerations, operation, advantages and limitations of these treatment technologies is provided in Table (2.1).

The process of adsorption is one of the techniques used in the treatment and removal of organic and inorganic components of water for several reasons: easy to apply, simplicity of design and feasibility in water purification (Gupta et al., 2011).

Overall, there is no single treatment option that can be considered the best method for removal of nitrate ions across all quality characteristics and for all systems.

Table (2.1): Potable water treatment options for nitrate management (Davis, 2012)

	Ion Exchange	Reverse Osmosis	Elerodialysis	Biological Denitrification	Chemical Denitrification
Treatment Type	Removal to waste stream	Removal to waste stream	Removal to waste stream	Biological reduction	Chemical reduction
Common Water Quality Design Considerations	Sulfate, iron, manganese, total suspended -solids (TSS), metals (e.g., arsenic), hardness, organic matter	Turbidity, iron, manganese, SDI, particle size, TSS, hardness, organic matter, metals (e.g., arsenic)	Turbidity, iron, manganese, TSS, hydrogen sulfide, hardness, metals (e.g., arsenic)	Temperature and pH, anoxic conditions	Temperature and pH
Pretreatment Needs	Pre-filter, address hardness	Pre-filter, address hardness	Pre-filter, address hardness	pH adjustment, nutrient and substrate addition, need for anoxic conditions	pH adjustment
Post-treatment Needs	pH adjustment	pH adjustment Remineralizaton	pH adjustment Remineralization	Filtration, disinfection, possible substrate adsorption	pH adjustment, iron removal, potential ammonia control
Waste/Residuals Management	Waste brine	Concentrate	Concentrate	Sludge/ bio solids	Waste media, Iron sludge
Water Recovery	Conventional (97%) Low brine (Up to 99.9%)	Up to 85%	Up to 95%	Nearly 100%	Not demonstrated full-scale
Advantages	Use in small & large systems, common application, multiple contaminant removal,	Multiple contaminant removal, TDS removal, use in small application, no chemical required, high quality product water	Multiple contaminant removal, higher water recovery (less waste), desalination, feasible	High water recovery, no waste brine or concentrate waste, potential for multiple contaminant	No waste brine or concentrate, high water recovery, and potential for multiple contaminant removal

	Ion Exchange	Reverse Osmosis	Elerodialysis	Biological Denitrification	Chemical Denitrification
	financial feasibility, ability to automate,		automation, no chemical usage,	Removal, limited chemical input, low sludge waste	
Disadvantages	High chemical use (salt), brine waste disposal, Potential for nitrate peaking, potential for disinfection byproduct	Membrane fouling and scaling, lower water recovery, operational complexity, energy demands, high capital and O&M costs, waste disposal	Energy demands, high system complexity, waste disposal, high costs, Skilled labour required, dependence on conductivity	Substrate addition, high system complexity, high monitoring needs, possible sensitivity to environmental conditions, risk of nitrite formation, high capital costs, post treatment requirements.	Inconsistency of nitrate reduction, risk of nitrite formation, reduction to ammonia, lack of full-scale systems, inexpensive capital cost, pH and temperature dependence, possible need for iron removal

2.3. Adsorption

2.3.1. Adsorption definition and operation

Adsorption is a surface phenomenon and is defined as a process of transfer or attach of soluble substance (organic or metallic material) in solutions to the surface of a solid material in low, medium and high coverage as show in Figure (2.2). Generally, adsorption can occur at any interface: e.g. gas- solid interface, liquid-solid interface (Al-Anber, 2011).
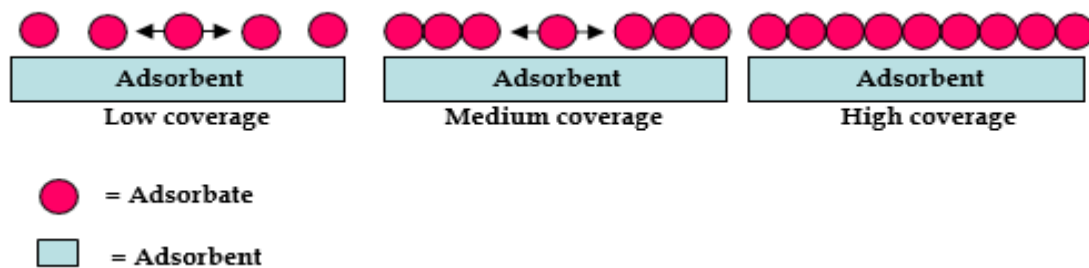
Figure (2.2): Types of coverage between adsorbent and adsorbate (Al-Anber, 2011)

Bonds and connection are formed between substance and solid surface through chemical or physical bonding. The substance (contaminant) that attaches to the solid surface or is removed from the liquid state is called the (adsorbate). The material that provides the solid surface is called (adsorbent). Different materials used as adsorbent in adsorption process such as:

- Natural inorganic materials (minerals, soils, limestone and building materials) (Bhatnagar, Kumar, & Sillanpää, 2011).
- Metal oxides and hydroxides (Zhou & Haynes, 2010).
- Zeolite (Widiastuti, Wu, Ang, & Zhang, 2011).
- Clay minerals such as kaolinite, mica, montmorillonite, vermiculite and layered Double hydroxides (Goh, Lim, & Dong, 2008).
- Ion exchange resins and fibres (Ku, Chiou, & Wang, 2002).

- Industrial by-products: Many types have been used to remove contaminants. Most adsorbents are in the by-product categories of the steel industry (e.g. slag), the generation of power plants (e.g. fly ash) and mining industry (e.g. red mud)(Bhatnagar et al., 2011; Bhatnagar & Sillanpää, 2011).
- Carbon materials: coal, biomass, wood, lignite and AC which is made from different materials include rice husks (D. Liu et al., 2016; Xu et al., 2013), date pits (Awwad et al., 2013), bamboo husk (Asberry et al., 2014), durian peel (Kamaruddin et al., 2012), olive waste (Hjaila et al., 2013), coconut coir pith (Shukla & Shukla, 2013), chestnut shell (Ertaş & Öztürk, 2013) and palm shells (Lim et al., 2015).

The adsorption process is known to proceed through three steps (Denizli, Say, & Arica, 2000):

1. Transfer of adsorbate from aquatic media to exterior surface of adsorbent, which mentioned as film diffusion).
2. Diffusion of adsorbate into pores of the adsorbent.
3. Interaction adsorbate with available sites and spaces on the interior surfaces bounding pore.

Soluble molecules are removed from the solution and uptake by the adsorbent through the adsorption process. Most particles are adsorbed on a large surface within the pores of the adsorbent. Few are relatively adsorbed on the outside surface of adsorbent. This transfer ends when the equilibrium is reached (Denizli et al., 2000).

The process of adsorption is one of the techniques used in the treatment and removal of organic and inorganic components of water for several reasons: easy to apply, simplicity of design and feasibility in water purification (Gupta et al., 2011).

2.3.2. Types of adsorption

Depending on the type of existing attraction forces that occur between the adsorbent and the adsorbate, the adsorption process can be divided into two main types: physical or

chemical adsorption. Table (2.2) presents the main features that distinguish between physical and chemical adsorption. Most adsorption processes are not purely physical and not pure chemical process, but usually a mixture of both (Faust & Aly, 2013).

Physical adsorption involving only relatively weak intermolecular forces, include both van der waals forces and electrostatic interactions comprising polarization, quadrupole interactions and dipole interaction. Chemical adsorption involves the formation of much stronger forces, that involve a true chemical bond between adsorbate molecule and the adsorbent surface (Faust & Aly, 2013).

Table (2.2): The comparative between physical and chemical adsorption (Faust & Aly, 2013)

Parameter	Physical adsorption	Chemical adsorption
Attraction force	Weak inter particle bond as van der waal forces	Strong attraction forces or chemical bond such as ionic bonds
Adsorption sites	Not site specific, the adsorbed molecules are free to cover the entire surface	Site specific, adsorbed molecule are fixed at specific sites
Temperature (adsorption heat)	Low heat of adsorption	Possible High heat of adsorption
Adsorption layer	Monolayer or multilayer	Monolayer only
Kinetics adsorption	Rapid, non- activated and fully reversible	Activated, may be slow and irreversible
Electron transfer	Not involve electron transfer, although polarization of sorbate may occur.	electron transfer leading to bond formation between sorbate and surface

2.3.3. Factors influencing adsorption

Adsorption is affected by the nature of adsorbent and adsorbate and experimental conditions (temperature, initial pH, contact time, adsorbent dosage, and initial adsorbate concentration).

2.3.3.1. Effects of surface polarity

One of the most important property of AC is that its surface slightly polar and in some cases is non-polar. This is due to surface oxide groups and inorganic impurities. This allows AC to adsorb the non-polar substances. We can say that the non-polar substances will be more easily adsorbed by adsorbent, if the adsorbent surface is non-polar or slightly polar (Al-Anber, 2011).

2.3.3.2. Effect of pH

pH study is an important parameter and considered as a major factor influencing adsorption. Zyoud, Nassar, El-Hamouz, and Hilal (2015) stated that nitrate adsorption from aqueous solution onto the surface of adsorbent is highly dependent on pH of solution. They studied removal of nitrate from aqueous solution via AC prepared from OS using conventional heating. They found that adsorption capacity increased at lower pH. It increased from 40% at pH 8 to 60% at pH 2. This is due to electrostatic attraction between nitrate and the positively charged surface site on the AC. Also, This is due in part to the strong competition between sorbates and protons and because of the effect of pH on functional groups of sorbates by ionization (Muhammad, Rodhi, & Hamid, 2012).

Machida, Goto, Amano, and Iida (2016) used the nitrogen doped AC to remove nitrate from aqueous solution. They mentioned that the lower the pH, the greater the absorption of negatively charged nitrate ions, because the adsorbent surface charge could become more positive in the acidic solution.

Namasivayam and Sangeetha (2005) observed that pH < 2 and pH > 10 achieved lower removal of nitrate. At pH < 2 lower removal is due to the competition of CL⁻ ions (from adding HCL to adjust the pH) with anions of nitrate for the adsorbent sites. At pH > 10 lower removal is due to the highly negatively charged AC surface sites, then the nitrate adsorption decreased due to electrostatic repulsion between the nitrate anion and negatively charged adsorbent surface.

2.3.3.3.   Effect of contact time

Contact time is considered an important factor which influences adsorption. Based on literature review, efficiency of removal is greater at high contact time. This is due to longer contact between solid and liquid, that enable better interaction between media and adsorbate (Foul, Aziz, Isa, & Hung, 2009). The removal of nitrate from aqueous solution by using AC prepared from OS is studied by Zyoud et al. (2015). She observed that nitrate adsorption percentage increasing when increasing time of treatment. Moşneag, Popescu, Dinescu, and Borodi (2013) investigated the ability of nitrate removal by utilization of granular activated carbon. They found the same result, the nitrate concentration of water decreased as adsorption time increased. Al-Anber (2011) stated that the adsorption capacity has high rate during the first time minutes until equilibrium is occurred. after that, there is no influence for increasing time. This is due to the decreased number of active sites on adsorbent surface.

Generally, it is observed that the rate of contaminants uptake by adsorption process increases with increase in contact time until equilibrium is occurred (Muthusamy, Venkatachalam, Jeevamani, & Rajarathinam, 2014).

2.3.3.4.   Effect of adsorbent dosage

In general, the efficiency of removal increased as the adsorbent dosage increases. This can be explained by the fact that higher dose of adsorbent mass in the solution, the greater contact surface offered to the adsorption, i.e. more exchangeable and active sites are available (Al-Anber, 2011).

Öztürk and Bektaş (2004) investigated the efficiency of nitrate removal from aqueous solution by adsorption using activated carbon, the effect of different values of dose (200, 400… 1000 mg) was examined and he observed that the removal percentage increased as the dose increases, which is due to the increase in adsorbent surface area of the adsorbents. The results also clearly indicate that the removal efficiency increases up to optimum dosage beyond which the removal efficiency is negligible.

2.3.3.5.   Effect of initial concentration

El-Said, Badawy, Abdel-Aal, and Garamon (2011) used the rice husk AC to remove Zn and Se from aqueous solution, they found that removal of metal ion decreased from 7.15 mg/g to 0.9 mg/g as the initial concentration decreased from 100 to 10 mg/g. they indicated that the available adsorption sites become fewer when the concentration of adsorbate become higher. Similar results have been obtained by (Kannan & Veemaraj, 2009)

(Al-Anber, 2011) stated that the existing sites of adsorption become fewer at high level adsorbate concentration, i.e. the adsorption efficiency decreases with increase in adsorbate concentration. This behavior is due to competitive diffusion process.

2.3.3.6.   Effect of particle size

Usually, smaller particle size implies a greater adsorption capacity this is due to the most of the internal surface of particles utilized for the adsorption Al-Anber (2011). Some of researchers use raw material in their original form (as shell or stone), but the majority of researchers use raw materials with a particle sizes between 1 mm to 2 mm. powder AC showed higher uptake rates than granular activated carbon. This is reported by Blázquez, Hernáinz, Calero, and Ruiz-Nunez (2005) , where the study examined effect of particle size on adsorption efficiency of Cd removal on activated carbon. The study showed that the removal percentage increase from 75% to 90% when the particle size decreased from 1mm to 0.35mm. this is due to the most of the internal surface of particles utilized for the adsorption. Al-Anber (2011) examined the effect of particle size on the removal efficiency. Three particle sizes (45, 125 and 250 µm). results demonstrated that the

maximum adsorption efficiency is occurred at particle size 45µm. Kannan and Veemaraj (2009) observed that the amount of Pb adsorbed decreases with the increases in particle size of adsorbent.

2.3.3.7.   Effect of temperature

Another important factor is temperature. Adsorption reactions are usually exothermic; therefore, the adsorption range generally increases with low temperature (Grassi, Kaykioglu, Belgiorno, & Lofrano, 2012). Mondal, Mishra, and Kumar (2015) investigate the effect of temperature on removal perecentage of Cd, the results showed that the maximum adsorption was at 30 ^{o}C and it decreased by increasing temperature.

(Zyoud et al., 2015) investigated the effect of temperature on removal percentage of nitrate on olive stone activated carbon. They found that the changing in removal percent of nitrate is not significantly.

2.3.4. Adsorption isotherm

Two essential parts are the fundamental requirements for the design of adsorption systems. These parts are adsorption isotherm and its kinetics. Adsorption isotherms (it also known as equilibrium data) is achieved when the capacity of the adsorbent materials is reached. Generally, adsorption isotherm calculates the adsorption or mobility capacity of adsorbent in either batch or continuous column studies (Al-Anber, 2011). Adsorbent capacity is calculated as concentration of substance (adsorbate) reduces between initial and at equilibrium conditions. It can be determined by using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2.1}$$

where, q_e (mg/g) is amount of adsorbate adsorbed per mass unit of adsorbent; C_o and C_e (mg/L) are the initial and at equilibrium concentrations of adsorbate; $V(L)$ is solution volume; and $W(g)$ is adsorbent mass used in the adsorption.

Langmuir and the Freundlich adsorption isotherms could be considered the most cited models to describe the adsorption isotherm in solid-liquid system. They relate adsorption density q_e (substance uptake per unit mass of adsorbent) to equilibrium concentration of adsorbate C_e (Al-Anber, 2011).

2.3.4.1.   Langmuir isotherm

Langmuir's isotherm is the simplest type of theoretical adsorption isotherms. Langmuir suggests that molecules uptake happens by monolayer adsorption on a homogenous surface, this means that no interaction between adsorbed molecules (each site can hold only one adsorbate molecule) (Jain, 2001; Vijayaraghavan, Padmesh, Palanivelu, & Velan, 2006). Langmuir's isotherm describes the adsorption process by using three assumptions: (i) strongly attract between surface of adsorbent and solution containing an adsorbate is occurred. (ii) adsorbate can be bind on every identical sites on adsorbent surface (every site can hold one adsorbed molecule). (iii) monolayer molecules attached to outer surface of the adsorbent (Alslaibi, Abustan, Ahmad, & Foul, 2013b). Langmuir's isotherm can be determined by using the following expression:

$$q_e = \frac{QbC}{1+bC} \qquad (2.2)$$

Where $q_e = \frac{x}{m}$ is the amount adsorbed for unit weight of adsorbent. Where x (mg) is the amount of adsorbed adsorbate, m (g) is the amount of adsorbent used, C (mg/l) is equilibrium concentration of molecule in solution, Q (mg/g) is Langmuir constant related to standard monolayer adsorption, b (l/mg) is Langmuir constant represents the degree of adsorption affinity related to sorption energy.

Several researches done on nitrate ions removal, which conformed to Langmuir modelm are summarized in table (2.3).

Table (2.3): Studies on nitrate adsorption that conformed to Langmuir isotherm

References	Adsorbent
(Paixão, Reck, Bergamasco, Vieira, & Vieira, 2018)	Babassu coconut
(Bhatnagar et al., 2008)	Coconut
(Katal et al., 2012)	Rice husk
(Machida et al., 2016)	Doped AC from petroleum pitch
(Moşneag et al., 2013)	peat grey
(Namasivayam & Sangeetha, 2005)	Coconut coir pith
(Y. Zhang et al., 2014)	Rice husk
(Demiral & Gündüzoğlu, 2010)	Sugar beet bagasse

2.3.4.2. Freundlich isotherm

Freundlich isotherm is considered the most usually used to describe the adsorption characteristics for the heterogeneous surface and applied to multilayer adsorption. It represents the initial surface adsorption followed by the condensation effect that result from strong interaction between adsorbent and adsorbate. In this perspective, the adsorption capacity is the summation of adsorption on all sites, with the stronger binding sites are occupied first, until energy of adsorption are exponentially decreased upon the adsorption completion (Adamson & Gast, 1967; Zeldowitsch, 1934).

Adsorption sites into Freundlich curves in the opposite way of Langmuir Isotherm are distributed exponentially with respect to adsorption energy. Heat in adsorption, in many cases, decreases in volume with increased adsorption. This decrease in temperature is logarithmic indicating that the adsorption sites are exponentially distributed with respect to adsorption energy (Alslaibi et al., 2013b).

Freundlich' isotherm does not indicate that adsorption stops when coverage is sufficient to fill a monolayer. Freundlich isotherm can be determined by using the following equation:

$$q_e = k_f \, C_e^{\frac{1}{n}} \tag{2.3}$$

where q_e (mg/g) is the amount adsorbed at equilibrium, C_e (mg/l) is adsorbate concentration, K_f (m/g)(l/mg)$^{1/n}$ is Freundlich constant related to maximum adsorption capacity and 1/n is Freundlich constant related to adsorption intensity of sorbent.

Several researches which investigated the efficiency of nitrate removal from aqueous solution are conformed to Freundlich isotherm are summarized in Table (2.4):

Table (2.4): Studies on nitrate adsorption that conformed to Freundlich isotherm

References	Adsorbent
(Öztürk & Bektaş, 2004)	Sepiolite, sepiolite activated by HCL from hand-carving waste
(Öztürk & Bektaş, 2004)	Slag, powder AC was originated from plants
(Widiastuti et al., 2011)	Natural zeolite
(Zyoud et al., 2015)	Olive stones

2.3.5. Adsorption Kinetics

Adsorption kinetics are very important in assessing the performance of a particular adsorbent and understanding the adsorption mechanisms. The process kinetics help to describe the adsorption rate of the absorbed substance on the AC and control the equilibrium time. Thus, the rate of treatment is one of the most important factors in the design of adsorption scheme (Chiron, Guilet, & Deydier, 2003; Lin & Wang, 2009) The most widely used kinetic models are the pseudo-first-order, pseudo-second-order and intraparticle diffusion (Y.-S. Ho & G. McKay, 1998; Y. Ho & G. McKay, 1998).

Pseudo-first-order model suggested by Lagergren (Alslaibi et al., 2013b). He explained that adsorption process is due to physisorption mechanism. The linear form of pseudo-first-order kinetic model is generally termed as follows:

$$Log\ (q_e - q_t) = Log(q_e) - \frac{k_1 t}{2.303} \tag{2.4}$$

Pseudo-second-order implies that adsorption capacity of adsorbed molecule depends on time (Bashir, Aziz, Yusoff, & Adlan, 2010).   And means that adsorption occur due to chemisorption-type mechanism (Krishni, Foo, & Hameed, 2014). A pseudo-second-order model described as:

$$\frac{t}{qt} = \frac{1}{k_2\ q_e^2} + \frac{t}{q_e} \tag{2.5}$$

where q_e (mg/g) is amount of adsorbate adsorbed at equilibrium; q_t (mg/g) is amount of adsorbate adsorbed at any time, k_1 (1/hr) is the equilibrium rate constant of pseudo-first-order, k_2 (g/mg hr) is the equilibrium rate constants of pseudo-second-order models and t (hr) is contact time.

Intra-particle diffusion model is generally characterized by a relationship between the concentration of solid phase concentration (q) and time square root (Weber & Morris, 1963). Adsorption as stated in section 2.3.1 is known to proceed through a multi-step process (three steps) involving transport of the solute molecules from the aqueous phase to the surface of the adsorbent particles followed by diffusion into the interior of the pores of adsorbent (Denizli et al., 2000). The intra-particle diffusion rate equation is expressed by the following expression:

$$q = k_3\ t^{0.5} \tag{2.6}$$

Where, K_3 (1/h) is the intra-particle diffusion rate constant, q (mg/g/h$^{0.5}$) is percentage adsorbate adsorbed, t (h) is contact period. The higher values of k_3 indicate an improvement in adsorption rate. While large values explain better adsorption mechanism, which means that attraction between adsorbent and adsorbate is very strong. Plot of q versus $t^{0.5}$ provides a straight line with slope equal to k_3 (Kobya, 2004).

2.4. Activated carbon

2.4.1. Definition

Activated carbon (AC) is a porous carbonaceous material with highly surface area, and in sometimes called as "material of the future", due to its excellent performance in a number of practical applications including treatment applications and adsorption process. The properties of AC structure have been shown to be effective in removing a wide range of both organic (Gupta et al., 2005) and inorganic (Gupta & Rastogi, 2008) pollutants dissolved in the aqueous medium (Bhatnagar et al., 2008) and/or from the gaseous media (K. Y. Foo & Hameed, 2010). AC has a high porosity, high surface reactivity, interaction, a large surface area and it also low cost (Martinez et al., 2006).

(Lowell, Shields, Thomas, & Thommes, 2012) stated that pore size distribution is one of the most important properties of activated carbon. The appropriateness of AC for difference adsorption process depends on the percentage in which pores of different sizes are present. According to the International Union of Pure and Applied Chemistry (IUPAC), AC pores classified by their sizes into three main groups: micropores (the average pore diameter < 2 nm), mesopores (the average pore diameter is between 2 - 50 nm), and macropores (the average pore diameter > 50 nm) as shown in Figure (2.3). Usually, AC with abundance of micropores are used for adsorption of small molecule contaminants in gas phase. AC with highly mesoporous are used for larger molecules adsorption in liquid phase (Y. Gao, Yue, Xu, & Gao, 2015).
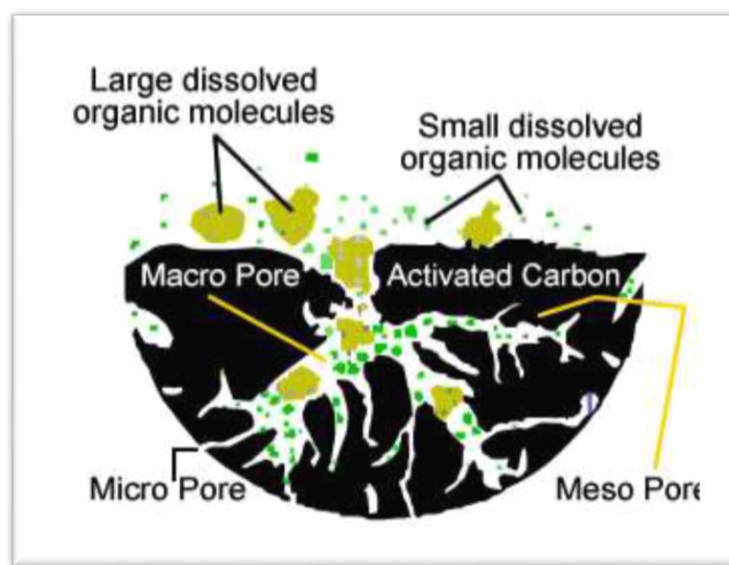
Figure (2.3): Activated carbon adsorbate mechanisms (IITK, 2014)

Lately, there are increasing demand of activated carbon, due to increase utility of the carbon materials in pollutants treatment and reduction. The companies in the world produce annually about 520,000 tons of activated carbon, 400,000 tons of which is used in water and air treatment (Chien et al., 2011)

2.4.2. Precursors for preparation of activated carbon

It can be said that AC can be produced from any inexpensive carbon-rich materials and containing low amount of inorganic materials. The use of commercial AC is still limited because of using natural and non-renewable materials such as coal or wood, and therefore, are still considered relatively expensive. In recent years, as a result of lower costs, there is growing interest in the production of AC from secondary agricultural products (agricultural by products) and waste materials, which are produced annually in large quantities (Arena et al., 2016). Agricultural by products can be categorized into two main groups. The first is soft, compressible waste with low density, such as soybean shells, rice husks, bagasse and so on. The second is hard, uncompressible waste with high density, such as dates stones, olive stones, apricots stones, pecan or walnut shells (Alslaibi, Abustan, Ahmad, & Foul, 2013a).

In recent years, different types of agricultural by-products are used as precursors in the manufacture of AC and then used in treatment processes. Some of these are summarized in Table (2.5)

Table (2.5): List of precursors used in manufacturing of activated carbon

precursors	Reference	precursors	Reference
rice husks	(Xu et al., 2013)	coconut coir pith	(Shukla & Shukla, 2013)
date pits	(Awwad et al., 2013)	Coconut shells	(Arena et al., 2016)
bamboo husk	(Asberry et al., 2014)	Moso bamboo	(Chien et al., 2011)
durian peel	(Kamaruddin et al., 2012)	Sugar beet bagasse	(Demiral & Gündüzoğlu, 2010)
olive waste	(Hjaila et al., 2013)	Bamboo dust	(Kannan & Veemaraj, 2009)
chestnut shell	(Ertaş & Öztürk, 2013)	Walnut shells	(J. Yang & Qiu, 2010)
spalm shells	(Lim et al., 2015)	Olive stones	(Alslaibi et al., 2013b, 2014a)

Olive is one of the most fruit growing crops in the world. Olive cultivation plays an important role in its rural economy, local heritage and environmental protection. The Middle East regions and Mediterranean counties are the largest producer of olive, providing 98% of the total cultivated area and 99% of the total olive oil production (Yakout & El-Deen, 2016) . The word production of olive oil reached 2.854 million tons for the current crop year (Sep.2017 – Aug. 2018). 15 million tons of OS were produced throw annually olive oil production (the International Olive Council, 2015). OS are cheap, quite abundant and rich in carbon. Therefore, it is considered one of the best materials used for the manufacture of AC and used it to remove pollutants from water and wastewater.

2.4.3. Preparation of activated carbon

The production of AC generally includes the following main steps: pretreatment of precursor, carbonization of precursor, activation of impregnated char. Pretreatment of precursor involves washing it several times to remove the dust, sand and other contaminants. then the precursor is crushed and sieved to obtain the desired diameter and then dried, so that almost all the moisture is extracted. The resulted dried precursor is kept and sent to carbonization process.

Carbonization process consist of several complex and consecutive reactions such as dehydrogenation, isomerization and condensation. Carbonization includes the thermal decomposition of the precursor, the elimination of the non-carbon species (volatile compounds) and the production of a constant carbon mass with primitive porous structure (small and closed pores are created) that usually called (char). These occur by heating in inert atmosphere in the absence of air (Yahya, Al-Qodah, & Ngah, 2015).

After that, AC are usually activated by two different methods: chemical activation and physical activation. Both processes are responsible in changing the shapes and sizes of char. The purpose of activation is to increase surface area, enlarge small pore diameters, create new pores, increase porosity and adsorptive capacity.

In physical activation, the char is placed under a high range of heat temperature from 700 to 1200 ^{o}C and activated with oxidizing agents such as stem, carbon dioxide CO_2 or mixture of them. The interaction between carbon atom and oxidized agents increases the surface area by creation new pores and enlargement of small pores. Physical activation is environmentally friendly since activation does not require chemical agents and there is no wastewater produced in this way. However, there are some disadvantages and limitations. It consumes a large amounts of energy, long time and yield is not high due to a large amount of carbon mass is eliminated during the activation process to produce a well-developed porous structure activated carbon. (Visvanathan, et al., 2009)

In chemical activation, char is impregnated with a chemical activation agent (mineral salts) such as KOH, NaOH, H_2SO_4, HCL, H_3PO_4, $ZnCl_2$, K_2CO_3, $NaCO_3$ and so on as

shown in Table (2.6). After that, activation is implemented with conventional heating as explained in section 2.4.3.1 or microwaved heating that will explained in section 2.4.3.2.

Chemical activation has more advantages and features than physical activation. It produces a larger surface area, higher yield, higher micro porosities, lower mineral matter content and needs lower heating temperature (Yahya et al., 2015). However, there are also some defects in chemical activation such as, there is a need to wash to remove the impurities that come from the activation factors as well as the corrosion properties of the factors (Lozano-Castello, Lillo-Rodenas, Cazorla-Amoros, & Linares-Solano, 2001)

Table (2.6): Common activation method for preparation of activated carbon

Activation method	Activation agent	Reference
Physical activation	Steam	(Moşneag et al., 2013)
	CO_2	(K. Yang et al., 2010)
	Mixed steam and CO_2	(K. Yang et al., 2010)
Chemical activation	$ZnCl_2$	(Demiral & Gündüzoğlu, 2010)
		(Theydan, 2018)
	NaOH	(Gupta et al., 2011)
		(Y. Zhang et al., 2014)
	H_2SO_4	(Hamoudi & Belkacemi, 2013)
	KOH	(K. Foo & Hameed, 2013)
		(Deng, Li, Yang, Tang, & Tang, 2010)
	H_3PO_4	(Yakout & El-Deen, 2016)
	$NACO_3$	(Jambulingam, Karthikeyan, Sivakumar, Kiruthika, & Maiyalagan, 2007)
	K_2CO_3	(K. Foo & Hameed, 2012a)
Physiochemical activation	$ZNCL/CO_2$	(Hu, Srinivasan, & Ni, 2001)
	KOH/CO_2	(Chowdhury, Zain, Khan, & Ashraf, 2011)

2.4.3.1. Chemical activation with conventional heating

Conventional heating method is usually used to prepare activated carbon. In conventional heating, the char is immersed in the chemical activation agent, then, the heating process

is carried out by placed the sample into an electric furnace in an inert atmosphere in the absence of oxygen at high temperatures ranging from 350 °C to 800 °C (Kilic, Apaydin-Varol, & Pütün, 2011). This method requires a long time to reactivate and consume more energy because it warms up the surface of the particle and then gradient to its interior.

Different types of agricultural by-products are used as precursors in the manufacture of AC by chemical activation with conventional heating. Some of These are summarized in Table (2.7)

Table (2.7): List of precursors used in manufacturing of activated carbon by chemical activation with conventional heating

Material	Chemical agent	References
Coconut	$ZnCl_2$	(Bhatnagar et al., 2008)
Date pits	$Ca(C_2H_3O_2)_2$	(Awwad et al., 2013)
Sugar beet bagasse	$ZnCl_2$	(Demiral & Gündüzoğlu, 2010)
Wood	$ZnCl_2$	(Acharya, Sahu, Mohanty, & Meikap, 2009)
Olive waste cake	H_3PO_4	(Hjaila et al., 2013)
Rice husk	KOH	(D. Liu et al., 2016)
Spanish anthracite	KOH	(Lozano-Castello et al., 2001)
Olive stones	KOH	(D. Liu et al., 2016)
Walnut shells	KOH	(Zabihi, Asl, & Ahmadpour, 2010)
Coconut coir pith	$ZnCl_2$	(Namasivayam & Sangeetha, 2005)
Olive stones	H_3PO_4	(Yakout & El-Deen, 2016)
Rice husk	NaOH	(Y. Zhang et al., 2014)

2.4.3.2. Chemical activation with microwave heating

In recent years, interest in the use of carbon materials (activated carbon, polymers, graphite and so on) has increased in a wide range of microwave assisted processes. This is due to the high capacity of carbon materials to absorb the microwave. In addition, it has received great interest because it can be used in commercial applications.

Over the past years, there has been an increase in the number of research and studies that merge the use of carbon and microwave heating compared to other traditional methods based on conventional heating. As shown in Figure (2.4), the number of scientific publications was very low until the late 1990s, but has risen significantly in the last decade, especially in the last five years (Menéndez et al., 2010).

Based on the interaction of the materials with the microwave, materials can be categorized into three main groups. Conductors (metals and alloys) are materials that reflect the microwave and cannot be penetrated. Insulators (fused quartz, teflon, glasses, ceramics and polypropylene) are low-loss material and highly transparent for microwave waves. The solvents (aqueous solutions and solvent solvents) are high-loss materials, which absorb the microwave radiation and transmit energy directly. The classification is shown in Figure (2.5) (Yuen & Hameed, 2009). At the same time, materials that absorb microwave radiation are called dielectrics, characterized by the possession of a few free charge carriers and displaying a dipole movement (Romano, Marra, & Tammaro, 2005).
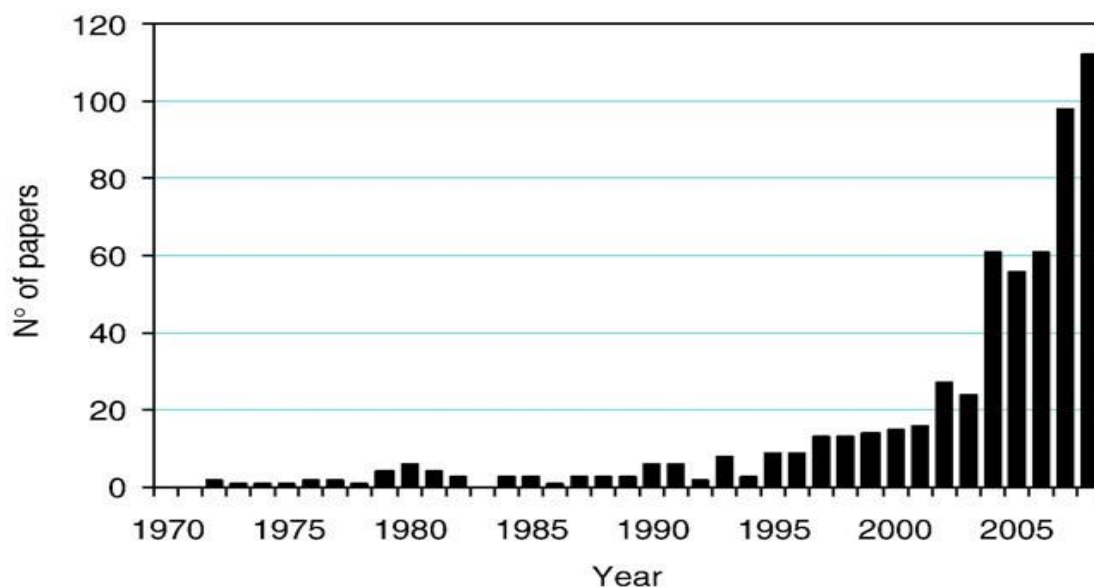
Figure (2.4): Number of research papers published on using carbon material with microwave-assisted processes (Menéndez et al., 2010)
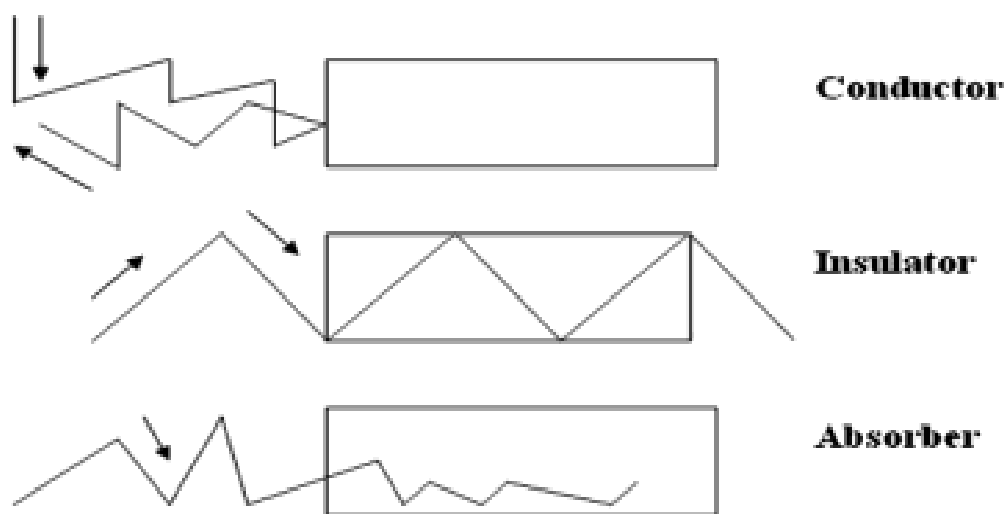
Figure (2.5): Microwave absorption characteristics for conductor, insulator and absorber (Yuen & Hameed, 2009)

Consequently, when microwaves are applied to the dielectric materials with an oscillating electric field, the dipole diodes inside the material will attempt to reorganize themselves and wrap around the applied field. As a result of this dipole movement, frictions are generated within the material and then this energy turns into internal heat (Romano et al., 2005).

During microwave heating, the massive thermal gradient from the inside of the particle turns to the surface (G. Zhang, Zhang, Deng, & Sun, 2011). These allow the microwave-induced interaction to proceed more quickly and effectively, resulting in saving the energy and short activation time as shown in Figure (2.6) (K. Yang et al., 2010). While, conventional heating is limited to heating the surface. The thermal gradient starts from the hot surface of the particle and moves towards the interior, which leads to difficulties in caloric transport (G. Zhang et al., 2011) .

Different types of precursors displayed in Table (2.8) used by previous researchers in the production of AC by applying chemical activation with microwave heating.
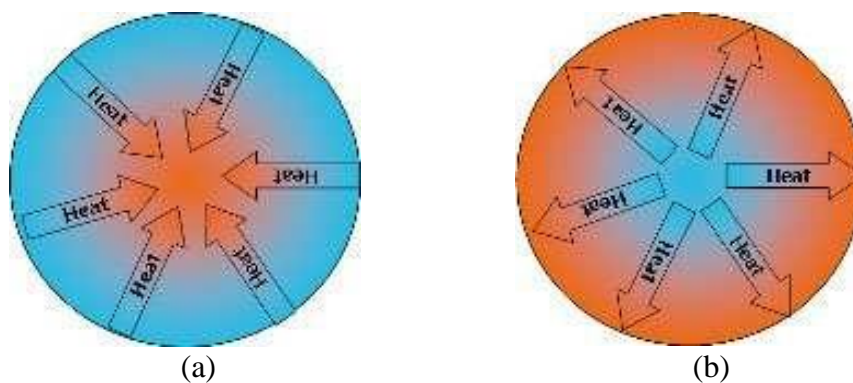
Figure (2.6): Quality comparison of temperature within samples heated by (a) conventional furnace heating and (b) microwave dielectric heating (X. Zhang & Hayward, 2006)

Table (2.8): Lists of precursor being used in the preparation of activated carbon by applying microwave technology

Precursor	Activating agent	References
Cotton stalk	H_3PO_4	(Deng, Zhang, Xu, Tao, & Dai, 2010)
bamboo	H_3PO_4	(Q.-S. Liu, Zheng, Wang, & Guo, 2010)
Pistachio nut shells	KOH	(K. Foo & Hameed, 2011a)
Cotton stalk	KOH& K_2CO_3	(Deng, Li, et al., 2010)
Apple waste	H_3PO_4	(Hesas, Arami-Niya, Daud, & Sahu, 2013)
Orange peel	K_2CO_3	(K. Foo & Hameed, 2012a)
Durian shell	NaOH	(K. Foo & Hameed, 2012b)
Olive stones	KOH	(Alslaibi, Abustan, Ahmad, & Foul, 2013c, 2014b)
Cocoa shell	$ZnCl_2$	(Saucier et al., 2015)
Oil palm	KOH	(K. Foo & Hameed, 2013)
Dates stone	KOH	(K. Foo & Hameed, 2011b)
Cotton stalk	$ZnCl_2$	(Deng, Yang, Tao, & Dai, 2009)

(Alslaibi et al., 2013a) studied the production of AC from OS with KOH as activating agent by using microwave heating. Effects on adsorption capacity were assessed. The results shown that the optimum conditions of microwave power, impregnation ratio (IR) (the ratio of weights of chemical agent to the precursor) and radiation time were 565 W, 1.87 and 7 min respectively. The surface characteristics of AC at optimum conditions were examined. The BET surface area, average pore diameter and total pore volume were 1280 m^2g^{-1}, 4.63 nm and 0.604 cm^3g^{-1}, respectively. Maximum adsorption on the OSAC was found for Fe^{+2} (62.5 mgg^{-1}).

Deng et al. (2009) used cotton stalk to prepare AC under microwave induced $ZnCl_2$ chemical activation. The results shown that optimized parameters were a radiation power of 560 W, a radiation time of 9 min and IR of 1.6 g/g. under which, yield of activated carbon, iodine number and amount of methylene blue were 37.92%, 972.92 mg/g and 193.5 mg/g, respectively.

K. Foo and Hameed (2013) utilized potassium hydroxide to optimize preparation of AC from oil palm via microwave radiation. The results shown that optimized parameters were a radiation power of 600 W, a radiation time of 10 min and IR of 1.75:1. Under optimum conditions, surface area and total pore volume were 895 m^2/g and 0.491 cm^3/g respectively. The amount of methylene blue adsorption was 343.94 mg/g. Another study by K. Foo and Hameed (2011b) used AC prepared from dates stones by microwave induced KOH chemical activation. They found that optimized parameters were a radiation power of 600 W, a radiation time of 8 min and KOH/C ratio of 1.75:1. They found that adsorption capacity was 316.1 mg/g, BET surface area was 856.23 m^2/g and total pore volume was 0.4680 cm^3/g.

AC prepared from bamboo with H_3PO_4 as activation agent was studied by using microwave radiation by Q.-S. Liu et al. (2010). The results show that the optimal activation conditions of microwave power, radiation time and IR were 350 W, 20 min and 1:1 ratio, respectively. Under the optimum condition, the maximum surface area was 1432 m^2/g and carbon yield was 48%. The found that conventional thermal process exhibits a

slower activation rate and lower carbon yield compared with microwave induced activation process.

Alslaibi et al. (2014a) stated that most common ranges of optimum condition (radiation power, radiation time and impregnation ratio) for preparation of AC from agricultural by-products by microwave induced chemical activation were radiation powers of 350 to 700 W, radiation time of 5 to 10 min and IRs of 0.5 to 2.

Recently, microwave induced chemical activation has been applied to prepare AC for removal several pollutants from aqueous solution using agricultural by-products. However, based to my literature review, no studies on nitrate removal using AC prepared by microwave technology have yet been done. In this research, we will carry out a set of experiments to verify the possibility and efficiency of removing nitrates from water by AC under microwave induced chemical activation.

2.4.4. Factors affecting activated carbon preparation

Radiation power (W), radiation time (t) and the impregnation ratio IR (g/g) are variables that affect characteristics of AC produced by microwave technology (K. Foo & Hameed, 2011b, 2013; Hesas et al., 2013)

2.4.4.1. Radiation power

The adsorption capacity increases with the increase of the microwave capacity because the porous composition is improving sufficiently. But with the increase of the microwave capacity to a certain level, excess energy can make a small amount of carbon burned, and the structure of the pores is destroyed.(Deng, Li, et al., 2010). Also, they noted that the iodine number and methylene blue number of AC gradually increases with the increase in the microwave power from 480 to 660 watts, and then decreases with the increase of the level of the microwave power to 720 watts.

Deng et al. (2009) reported that the yield of AC increased gradually from 27.3% to 32.4% with the increasing of microwave power from 400 W to 560 W, and then decreased to

32.2% with increasing of the radiation power to 640W. Also, the iodine number and the amount of methylene blue had the same behavior. The probable cause was that the higher energy was offered to the samples with increasing power the level, the more active sites and pores on the samples.

K. Foo and Hameed (2012a) noted the similar behavior of microwave radiation power. They investigated the preparing AC form orange peel by using microwave technology. the effect of microwave power on the adsorption uptake capacity and yield of carbon were studied. They reported that with the low microwave power between 90 W and 180 W, the pore structure was not sufficiently developed, and the adsorption rate and yield remained constant without change. At higher microwave power from 180 W to 600 W, pore width was increased and micropores and mesopores of carbon were formed. Also, the adsorption uptake capacity and BET surface area were increased. Nevertheless, adsorption capacity and yield decreased gradually at a high radiation power of 800 W. This is due to the fact that over gasification may occur with a detrimental effect that leads to the destruction of carbon pore structure (K. Foo & Hameed, 2012a).

Hesas et al. (2013) investigated the effect of microwave radiation power on adsorption uptake capacity of AC prepared from apple waste. The results shown that the adsorption capacity increased from 49.6 to 80.23% when the microwave radiation power was increased from 550 to 700 W. This indicates that the high microwave power improves the development of pores on carbon in activation stage.

However, preparation of AC via microwave radiation is highly proportional to the microwave power. At the same time, the rate of carbon loss has increased in proportion to power levels, this is due to the intense reaction at the high microwave power level, that causes rapid dehydration and degradation of materials (Deng et al., 2009).

2.4.4.2. Activation time

Activation time is another important factor affecting the adsorption uptake capacity and carbon yield. Increasing the activation time would cause in enhancing the adsorption

uptake capacity. This due to opening and enlargement of pores on and inside the surface of AC (K. Foo & Hameed, 2012b). Hesas et al. (2013) stated that prolong microwave radiation time might cause continuous pore enlargement, but at a longer time apparent pore structure destructed and a slight drop in adsorption.

Hesas et al. (2013) investigated the effect of activation time on adsorption uptake capacity of AC prepared from apple waste. The results shown that the adsorption capacity increased by approximately 20% when the activation time was increased from 10 to 15 min at constant microwave power of 550 W. This indicates that the high activation time improves the development of pores and active sizes on carbon in activation stage. At microwave power of 700 W, when the activation time increased from 10 to 12.5 min, the adsorption was increased, then decreased from 12.5 to 15 min. This may be due to the destruction of small pores due to exposure to a long period of microwave radiation

The effect of activation time on the preparation of AC was investigated by Q.-S. Liu et al. (2010) . The results showed that activation time significantly affected the development of pore structure and surface area of activated carbon. They reported that with activation time going on, both micropores and mesopores increased, implying that the pores were formed and enlarged. This behavior continued until activation time 20 min. After that, a slow increase in the pores got up to 30 min. This phenomenon shows that the formation of new pores became less important as the process of activation continues. As the activation process continues, the reduction in small pores has been observed. This may be due to the destruction of micropores due to exposure to a long period of microwave radiation. They also found that the yield of AC decreased gradually from 58.6% to 45.3% with the increasing of microwave radiation time from 5 min to 30 min, due to the continuous loss of weight with increase of radiation time. Deng et al. (2009) also observed the same results in the preparation of AC from cotton stalk under microwave radiation.

However, preparation of AC via microwave radiation is highly proportional to the microwave radiation time (activation time). The higher the microwave radiation time, the more active pores and sites are formed on and inside the carbon surface. Therefore, adsorption capacity of AC will increase with the prolongation of microwave radiation.

However, when radiation time reaches a certain point, the carbon pores will be burned by heating the microwave radiation, thus reducing carbon adsorption capacity (Deng et al., 2009).

2.4.4.3. Impregnation ratio

The impregnation ratio (defined as the ratio of the weights of chemical agent and the precursor) is one of the factors that affect the activation process, which plays an important role in the creation of new pores and enlargement of pores exist. Thus contributing to improved surface area and adsorption capacity.

The effect of IR of $ZnCl_2$ on the preparation of cotton stalk activated carbon CSAC investigated by Deng et al. (2009). The results showed that the increase in the rate of impregnation from 0.8 g/g to 1.6 g/g led to an increase in both yield and adsorption capacity of activated carbon. This is due to the effect of $ZnCl_2$ that is to inhibit the release of volatile substances, resulting in increased yield and adsorption capacity. Later, with the increase of the IR to 2.0 g/g, the adsorption capacity and carbon yield decreased. This is because the chemical agent $ZnCl_2$ plays the role of dehydration factor during activation. It prevents the formation of tar or other liquids that can clog up carbon pores, thus preventing the transmission of volatile matter through the pores, and the ability of adsorption and yield decreased. Similar results were reported by (Deng, Li, et al., 2010). They studied the effects of IR on preparation of AC from cotton stalk by using chemical activation via microwave radiation. They observed when KOH/C ratio was increased from 0.4 to 0.6 g/g, the adsorption uptake capacity of iodine number and methylene blue were increased. Increasing ratio of KOH/C from 0.6 to 1.4 g/gm the adsorption capacity was decreased gradually.

From the discussions mentioned above, the microwave radiation power, activation time and the IR had important effects on the yield and the adsorption capacity of the AC from agricultural by products with chemical activation by microwave radiation.

2.4.5. Characteristics of activated carbon

AC is characterized by its physical and activity properties, both of which are very important in determining which carbon is produced. The important physical properties are surface area, ash content, product density (bulk density), mesh size and corrosion resistance (Ashour, 2013).

Activity characterization are key indicators of potential carbon performance to remove water pollutants. An important characterization tool used to determine the adsorption uptake capacity of carbon to remove a molecular adsorbate is the distribution of pore size. Pore size distribution determines the size of the pores available on and into carbon surface over three several pore sizes (micro-pores, meso-pores and macro-pores) (IITK, 2014).

The following are the standard methods used to measure these characteristics, while in some properties an alternative rough methods were used due to the lack of some of devices and equipment in the Gaza Strip, the used method will be explained in the next chapter.

2.4.5.1. Surface area

It is defined as the total area available for absorption. The surface area is determined using Micromeritics ASAP 2020 volumetric adsorption analyzer, which is based on N_2 gas adsorption at 77 K. The system is operated by measuring the amount of gas absorbed on a solid surface. Surface area was measured from adsorption isotherm using the Brunauer-Emmett-Teller equation (BET) (Alslaibi et al., 2013a).

Due to the shortage of equipment in the Gaza Strip and the high cost of the BET test, a rough test method is available using the Acetic Acid Isotherm Test, which can be summarized in the following steps. Ashour (2013) determined the surface area using the acetic acid method.

- AC is washed many times with distilled water and dried for 24 hours at 105 °C until reaching a constant weight.
- Six glass bottles are treated with acetic acid (0.5 M), then rinsed with distilled water and dried with oven.

- Six samples of AC each 1 gram are placed in pretreated bottles.

- A range of acetic acid concentrations between 0.05 and 0.16 M per 100 ml were prepared and placed in the bottles.

- The bottles are periodically shaken at 25 $^{\circ}$C for 60 min until they reach equilibrium.

- The samples are filtered and eliminated the first 10 ml and titrate using 0.1M NaOH and Phenolphthalein,

- The number of moles adsorbed at equilibrium for all samples (C_e) are measured, and the total number of adsorbed moles per gram of AC are calculated by the equation: $N = (C_o - C_e) * V / g$, where $V(cm^3)$: sample size, g (g) grams of activated carbon, C_o (mole): initial concentration, C_e (mole): Final concentration at equilibrium).

- A graph for C_e Vs C_e / N is plot, according to the equation $C_e / N = C_e / N_m + 1 / kLNm$. where $1 / N_m$ is the slope of the curve and giving a number of adsorbed acetic acid moles by the gram of activated carbon, $1 / K_L$ is a constant equals the intersection of the Y axis.

- Assuming a mono layer of acetic acid and knowing the molecule as 2.1 x 10^{-19} m^2/molecule and Avogadro number is $6.02x10^{23}$ molecule /mole, the total area is calculated.

2.4.5.2. Bulk density

Bulk density is the mass of the volume unit of the material in the air, including the pores and spaces (voids) between the particles of the material and expressed in kg/m^3. Bulk density depends on the form and size of particles and the density of individual's particles. The standard method for measuring the bulk density are as specified in DIN ISO 787.11 and ASTM D 2854. It can be summarized as follows:

- Dry sample shall be prepared after drying in the oven at 105 $^{\circ}$C for 24 hours to reach the constant weight,

- In a graduated cylinder installed in the vertical tapping device with frequency 250 +/- 15 taps / min capacity 3 mm, 200 ml of AC is placed to avoid entraining air.

- The top is flattening and cycle 1250 times, the volume is read.

- Repeat the procedure until the difference between the two observation is less than 2 ml (V)

- Weight of cylinder content to the nearest 0.10 g (M)

- Bulk density Db = 1000 M/V

2.4.5.3. Ash content

Typically, the ash content of the Activated Carbon is dependent on the ash content of the precursor. The ash is a non-carbon material, which is usually mineral additive that is not attached to the surface of the carbon. Ash content measurement is determination of residual material behind carbonization and activation. The higher ash content the lower effective activated carbon. Ash content can be measured in accordance with ASTM D 2866-70 as follows:

- Dry enough sample of AC in oven until reach a constant weight at 150 $^\circ$C minimum of three hours.

- Ignite the crucible in the muffle furnace for 1 hour at 650 $^\circ$C, and then cool to room temperature and determine the crucible weight (G)

- Place sufficient amount of AC and weight both the AC and crucible to the nearest 0.1 g (F).

- Place the content in the furnace at 650 $^\circ$C to ash the content, it may take from 3 to 16 hours, until a constant weight (B) is reached.

- Ash content is given by Ac = 100 (B-G) / (F-G)

2.4.6. Application of activated carbon in aqueous solution treatment

A variety of methods have been used to remove a number of contaminants from water or wastewater, such as ion exchange, electrodialysis, decomposition, reverse osmosis, ion exchange, evaporation and adsorption. AC is considering one of the most important

adsorbents because of its high efficiency in removing organic (Gupta et al., 2005) and inorganic compounds (Gupta & Rastogi, 2008). However, the use of commercial AC is still limited because of using natural and non-renewable materials such as coal or wood, and therefore, are still considered relatively expensive (Arena et al., 2016).

A number of researchers have investigated the efficiency of the use of AC prepared from agricultural by-products to remove organic and inorganic compounds, as well as their water / wastewater treatment. The key parameters affecting the removal of contaminant are the pH, carbon dose, the contact time, initial adsorbates concentration and temperature.

AC has been used to remove nitrate from water. However, the number of studies on the use of AC in nitrate removal is still low compared to the elimination of other forms of contaminants. The reason may be that nitrates are highly soluble in water, so the removal ratio of nitrates will be low or slow (Batheja et al., 2009)

Sugar beet bagasse AC (SBAC) was prepared by Demiral and Gündüzoğlu (2010) with use of chemical activation with $ZnCl_2$ as chemical agent. Effects of IR and activation temperature were investigated. Optimum AC was obtained with use of a 700 °C activation temperature, and an IR of 3. This resulted in an SBAC surface area of 1862 m^2/g and pore volume of 0.966 cm^3/g. The effects of pH, contact time and temperature on the removal efficiency of nitrate from water using SBAC were investigated, the results shown that the initial pH value didn't affect removal percentage significantly, and when the temperature increased the adsorption capacity increased.

Nitrate removal from aqueous solutions via AC prepared from OS by $ZnCl_2$ chemical activation as adsorbent, was investigated by Zyoud et al. (2015). She investigated the adsorptive properties of OSAC in terms of adsorbent dosage, contact time, pH, temperature and nitrate initial concentration. She found that with a decrease in pH, the adsorption of nitrate increased, so lower values of pH are favorable for removal of nitrate. The effect of temperature on adsorption indicated that the temperature slightly affected adsorption capacity. The results indicated that adsorption capacity of nitrate was better represented by the Langmuir model. The equilibrium time for nitrate adsorption is 60 min.

Bhatnagar et al. (2008) investigated the production of AC from coconut by $ZnCl_2$ chemical activation. The nitrate adsorption on coconut AC was studied in terms of contact time, initial concentration of adsorbate, pH and temperature by batch mode adsorption experiments. The adsorption capacity was found 10.2 mg/g. the adsorption results conform best fit to the Langmuir model. The maximum removal of nitrate from water was occurred at IR of 2:1 and temperature of 500 $^{\circ}$C.

Nitrate removal from aqueous solution by adsorption onto powdered AC was studied by (Öztürk & Bektaş, 2004). They investigated the adsorptive properties of AC in terms of adsorbent dosage, contact time and pH. The equilibrium time was found to be 45 min. An increase in pH and adsorbent dosage increased the removal percentage of nitrate.

2.5. Olives production

Olive is one of the most fruit growing crops in the world. Olive cultivation plays an important role in its rural economy, local heritage and environmental protection. The Middle East regions and Mediterranean counties are The largest producer of olive, providing 98% of the total cultivated area and 99% of the total olive oil production (Yakout & El-Deen, 2016) . The word production of olive oil reached 2.854 million tons for the current crop year (Sep.2017 – Aug. 2018). 15 million tons of OS were produced annually throw process of olive oil production (the International Olive Council, 2015).

The demand for olives has increased significantly in recent decades, largely in response to the growing public awareness of the health benefits associated with olive oil. Some useful attributes of olive oil include being a source of antioxidants, vitamin E, and monounsaturated fats, which help prevent cardiovascular disease. Figure (2.7) shows the increase in production and demand for the period from 1990 to 2016 (OLIVAE,2016).
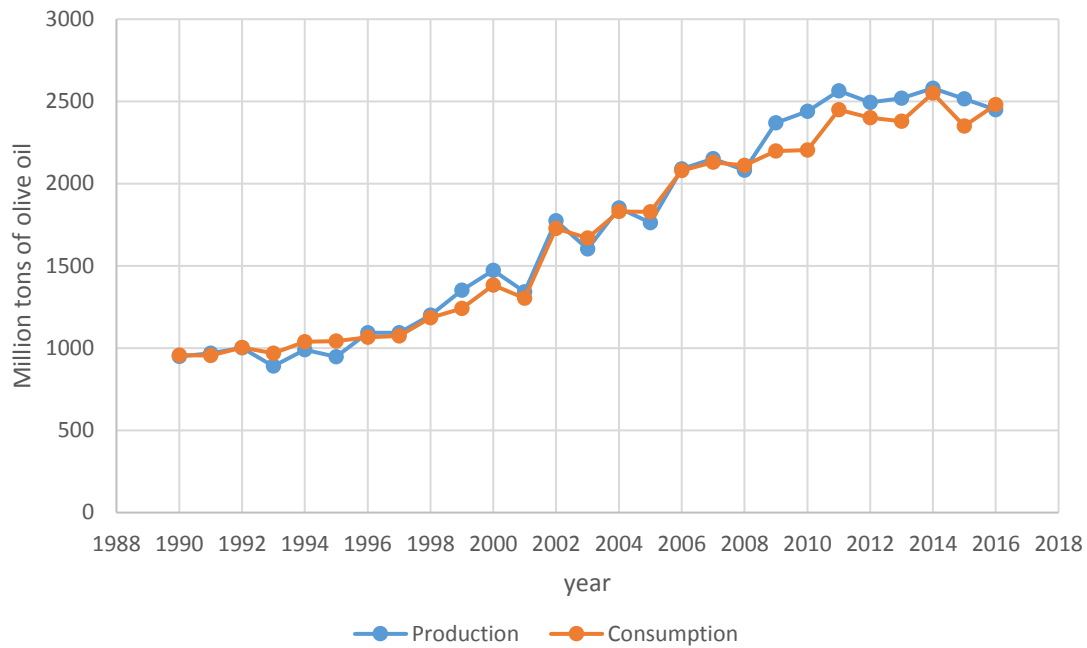
Figure (2.7): Olives oil production & consumption (OLIVAE, 2016)

2.5.1. Olive by-products

Unfortunately, byproducts produced during the manufacture of olive oil in millers are a serious environmental problem. Traditionally, olive mills produce olive oil and two kinds of waste products: wastewater and solid waste (Pütün, Uzun, Apaydin, & Pütün, 2005). The solid waste of olive oil extraction, which is approximately 35% of the weight of the olive fruit, consists of stones, skin and pulp of olive fruits (Doymaz, Gorel, & Akgun, 2004). Most olive wastes are dumped in the environment without any management, where they may be contaminated by fungi or toxic compounds or used as source of energy (Pütün et al., 2005).

OS consist of a group of material such as hemicellulose, lignin, lignocellulosic and cellulose material. The OS also contains a large proportion of fats, carbohydrates, proteins, water-soluble and a small (but active) fraction of hydro soluble phenolic material (Rodríguez et al., 2008).

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2.5.2. Advantages of olive stones as precursor for activated carbon

OS can be considered as one of the most important agricultural byproducts using in production activated carbon This is due to its high efficiency in removal and because its low cost, quite abundant and rich in carbon (Moreno-Castilla, Carrasco-Marín, Lopez-Ramon, & Alvarez-Merino, 2001). Furthermore, it appears that carbon based on the OS has special advantages such as mechanical stability (Moreno-Castilla et al., 2001), Durability, low swelling in the water medium and low sulfur and ash content (El-Hamouz, Hilal, Nassar, & Mardawi, 2007). Some of the recent studies have been investigated the AC preparation from different olive by-products. Michailof, Stavropoulos, and Panayiotou (2008) investigated using olive husk for the producing of AC by chemical activation with potassium hydroxide and was used for adsorption of polyphenol mixtures. OS were also used to prepare AC by chemical activation via microwave radiation and was used for heavy metals removal from wastewater (Alslaibi et al., 2013a).

OS have been used as raw material to produce AC by both chemical and physical activation methods using different activating agent such as $ZnCl_2$ (Zyoud et al., 2015) , phosphoric acid (Yakout & El-Deen, 2016) , potassium hydroxide (Alslaibi et al., 2013a) and carbon dioxide and steam (Román, González, González-García, & Zamora, 2008).

AC prepared from OS was used to remove different materials from aqueous solution such as uranium and thorium (Kütahyalı & Eral, 2010), heavy metals (Alslaibi et al., 2014a), textile dying effluent (Rosas, Bedia, Rodríguez-Mirasol, & Cordero, 2009), cadmium ions (Alslaibi et al., 2013b), copper ions (Baccar, Bouzid, Feki, & Montiel, 2009) and chromate ions (El-Hamouz et al., 2007). In this work, AC prepared from OS by chemical activation via microwave radiation is used in nitrate removal from water.

2.5.3. Olives mills in the Palestine

Palestinian Central Bureau of Statistics (PCBS) stated that there are 295 olive mills in Palestine in 2017, 274 working in good condition and about 21 of them temporarily closed. 258 of these mills are fully automatic and 16 semiautomatic or conventional (Palestinian

Central Bureau of Statistics PCBS, 2017). Figure (2.8) shows the distribution of the olives mills in Palestine
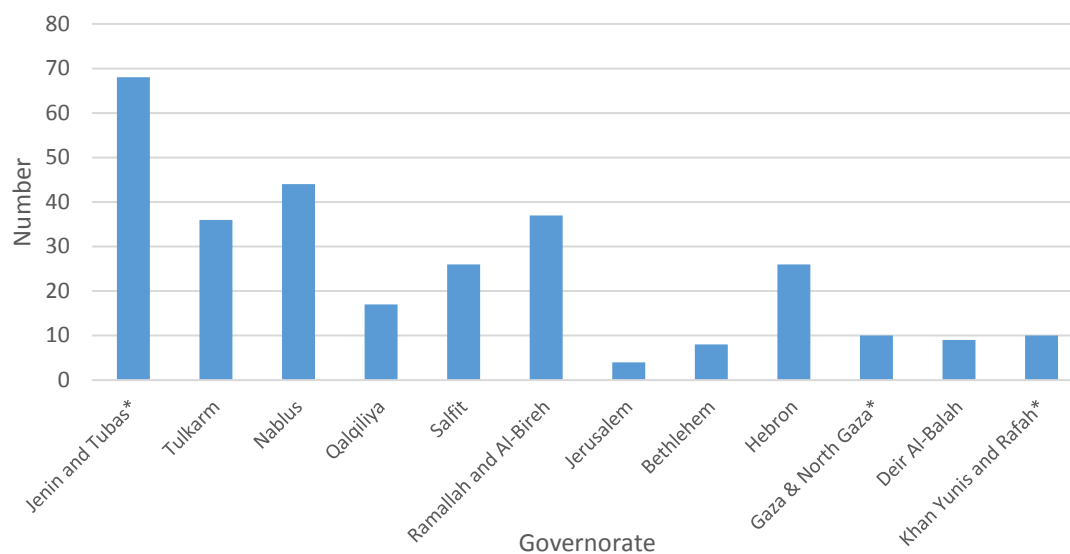
Figure (2.8): The distribution of the olives mills in Palestine (Palestinian Central Bureau of Statistics PCBS, 2017)

PCBS showed that the quantity of olives supplied to the mills in Palestine amounted to 87,800 tons. The amount of oil extracted from olive 19,532 tons. Thus, the percentage of oil extracted from olives reached 22%.

Chapter 3

Research methodology

Chapter 3
Research methodology

3.1. Introduction

Experimental work and laboratory procedures are explained in this chapter. Equipment, tools, methods, chemicals, tests and analytical methods are presented. Procedures of AC production, Operational parameter and characterization of AC are also explained. Furthermore, isotherms, kinetics and batch adsorption studies are discussed. All experiments were conducted in triplicate to get consistent results.

3.2. Materials and equipment

During the research, reagents and chemicals were used in experimental tests are summarized in Table (3.1). The general equipment and tools were used in this work are listed in Table (3.2). All of these regents, chemicals, equipment and tools were obtained from the Earth Sciences and Environment Laboratory at Islamic University of Gaza.

Table (3.1): List of reagents and chemicals used in present research

Chemicals/reagents	Formula	Mol. Weight (g/mole)	Assay	Source	Usage
Potassium Nitrate	$K\,NO_3$	101.103		HIMEDIA RM 402	To prepare nitrate stock solution
Concentrated sulfuric acid	H_2SO_4	98.079	98%	HOMED	To keep nitrate stock solution concentration
Nitrogen	N_2	28.0134	99.9%	Al-Ghusain Company for Gases, Trade and Industry	To form an inert atmosphere for carbonization and activation process
Acetic acid	CH_3COOH	60.025	99%	Chempal Company	To determine surface area of AC
Zinc chloride	$ZnCl_2$	136.286	97%	HIMEDIA RM 696	Activating agent
Hydraulic acid	HCl	36.49	37%	CARLO ERBA UN1789	pH adjustment
Sodium hydroxide	$NaOH$	39.997	>99%	Laboratory Rasayan	pH adjustment

Potassium hydrogen phthalate KHP	C_8H5KO_4	204.22	98%	FLINN SCIENTIFIC	Standardization of NaOH solution
Phenolphthalein ph.ph	$C_{20}H_{14}O_4$	318.32		SCIENCE Company	As indicator in acid-base titrations
Buffer solution with pH values of 4&7				Thermo Fisher Scientific	To calibrate pH meter

Table (3.2): List of equipment used in present research

Equipment	Brand/ model	Usage
Oven	Climas – 6086	Sample drying
Muffle furnace	BIFA laboratory furnaces multi stage- model MS 8-36	Carbonization of precursor
Microwave oven	DURABRAND- Model XB2316	Activation of char
pH meter	ADWA KFT AD11	pH measurement
Shaker water bath	YCW-012	Batch adsorption studies
Analytical balance	LAC.114	Weight measurement
Spectrophotometer	CT-2200	Nitrate measurement
Scanning electron microscope SEM		Determine surface morphology of activate carbon
Vibration machine	DRAGON LAB SK-330- Pro	Measuring bulk density
Sieve		To ensure consistency of size
Shaker	DRAGON LAB SK-330-Pro	Batch adsorption studies

3.3. Experimental work

Experiments were conducted at the Earth Sciences and Environment Laboratory at Islamic University of Gaza. Laboratory work has been divided into two main stages: the first stage is to prepare AC from crushed OS through pretreatment, then carbonization and finally activation. The second phase is the use of AC to remove nitrates from the synthetic water sample using the batch study method, taking into account several variable factors in order to reach the optimum state of removal. The flowchart of the experimental work is shown in Figure (3.1).
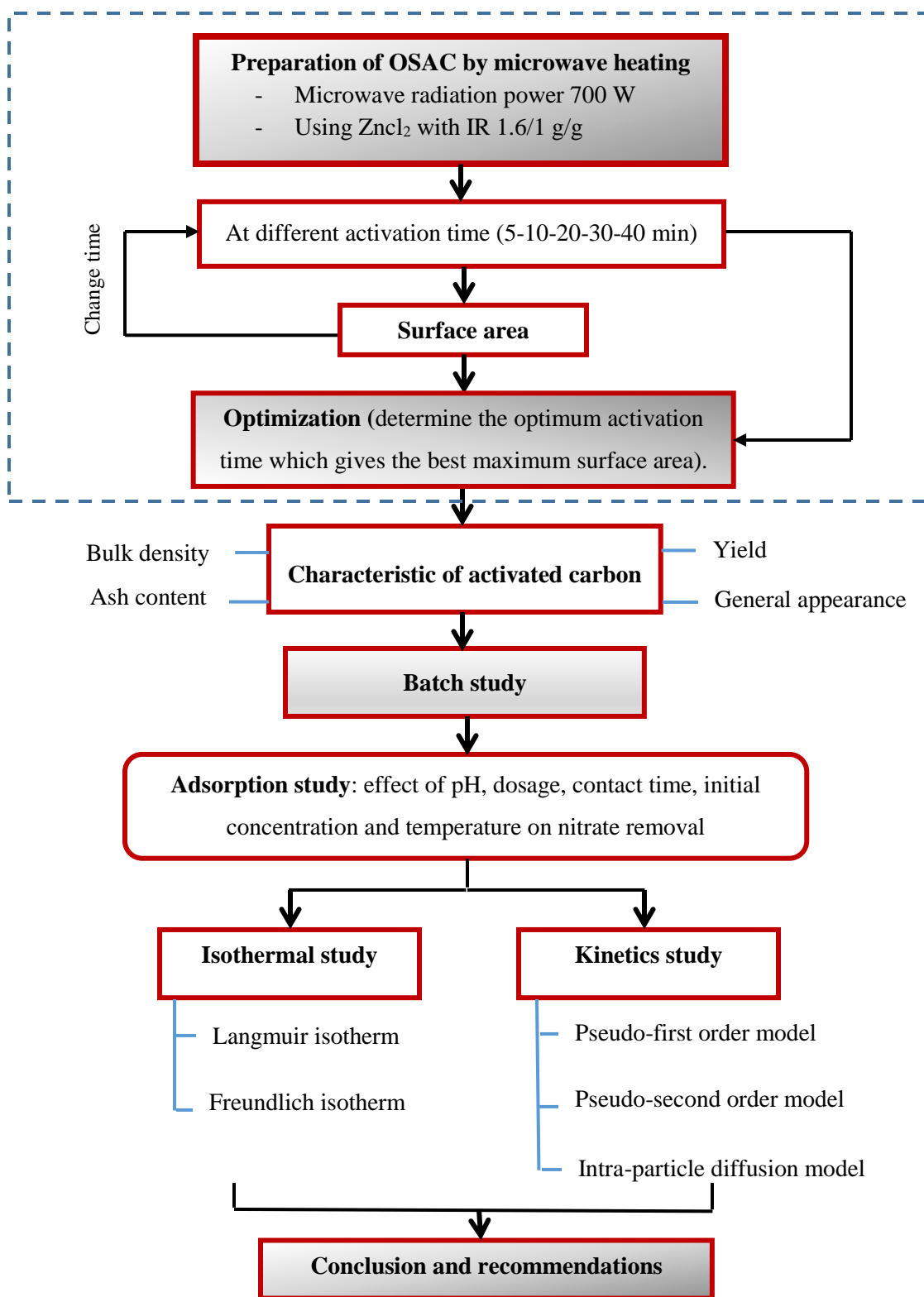
Figure (3.1): Schematic diagram showing the sequence of the experimental work in research

3.3.1. Producing activated carbon

As mentioned in section 2.4.3, AC production generally includes three main procedures: precursor collection and pretreatment, carbonization of precursor and the activation of char. In this section, we will explain the procedures followed to manufacture the AC from crushed OS.

3.3.1.1. Olive stone collection and pretreatment

As stated in Section 2.5.3, there are 29 olive factories in the Gaza Strip (PCBC, 2017). In the Gaza Strip, the season of olive harvesting and oil producing begin in September and end in November each year. The sample of OS were collected from the Alasar olive mill in Gaza City.

Samples were taken to the laboratory, pretreatment of samples involves washing it several times with hot and cold distilled water to remove the dust, sand and other contaminants. The crushed OS are separated from the grinded leaves and pomace by floating them in water, where the crushed stones settle and other parts float and scraped until the crushed stones are become cleaned. After that, the samples were dried in the oven at 105 ^{o}C for 24 hours with stirring periodically to ensure drying of all particles surfaces and internal pores and to remove all the moisture content. Once drained, it was sieved to obtain the desired particle size (1.7- 2.8 mm). The resulted dried precursor samples were kept and stored in a well-sealed glass jar until use as shown in Figure (3.2).

Figure (3.2): Pretreatment of crushed OS

3.3.1.2. Carbonization of the precursor

Following the same literature of (K. Foo & Hameed, 2011b, 2012a)for carbonization of the OS at a temperature above $700\,^{\circ}\mathrm{C}$ under purified nitrogen (99.99%) . BIFA laboratory muffle furnace multi stage (model MS 8-36) was used in carbonization process. Some of modifications have been made; reactor is made from a stainless steel with dimensions 20 cm length, 14 cm width and 10 cm high with a threaded cap. 6mm pipe from stainless steel is connected to the reactor to allow N_2 gas enter the reactor and release of volatile gases resulting from the carbonization process. The reactor in the furnace is connected to the N_2 source (40 liters at 200 bar pressure) through a flow scale of 0 to 25 L/min. The final arrangement of the electrical muffle furnace as described above is illustrated in Figure (3.3).

Figure (3.3): Electricity muffle furnace with modification

Carbonization was carried out by loading 400 g of dried precursor in a stainless steel reactor placed in a muffle furnace at 700 °C for one hour under purified N_2 (99.99%) with flow 300-500 cm^3/min. N_2 flow is to release volatile matter and produce chars with rudimentary porous structures. After carbonization, the whole quantity was sieved and the size of 1 to 2 mm was taken as a target size (K. Foo & Hameed, 2013).

As explained in section 2.4.3, carbonization process includes the thermal decomposition of the precursor, the elimination of the non-carbon species (volatile compounds) and the production of a constant carbon mass with primitive porous structure (small and closed pores are created) that usually called (char). This throw several complex and consecutive reactions such as dehydrogenation, isomerization and condensation. These occur by heating in inert atmosphere in the absence of air (Yahya et al., 2015)

During the carbonization process, a series of observations were recorded:

- After 30 min from the beginning, i.e. when the temperature reaches 300 °C, the resulting gases from the process of carbonization began to rise. The exit of the gases continued and was loaded with tar until the temperature reached 700 °C.
- The gas exit stopped after 20 min of reaching the temperature 700 °C.
- System for gases treatment was designed to reduce the risk of gas emissions as shown in the Figure (3.4).

Figure (3.4): Carbonization process with reducing risk of gases

3.3.1.3. Activation of the char

Char chemical activation via microwave heating was carried out by using commercial microwave (700 W, 2450 MHz, Durabrand XB2316, UK) with some modifications as shown in Figure (3.5). The microwave contains a power controller to determine the desired power level and a timer to select different exposure times of activation. N_2 gas was supplied to the system at constant pressure which was adjusted using the pressure regulator. Gas flow meter was used to measure the N_2 flow rates supplied to the microwave. Teflon tubes were used as pipes within the system (the pipes responsible for the inlet of N_2 gas and the release of volatile gases resulting from the activation process). In addition, two flasks filled with water and placed next to the microwave to ensure inlet flow of N_2 and filtration of volatile matter before releasing into the air.
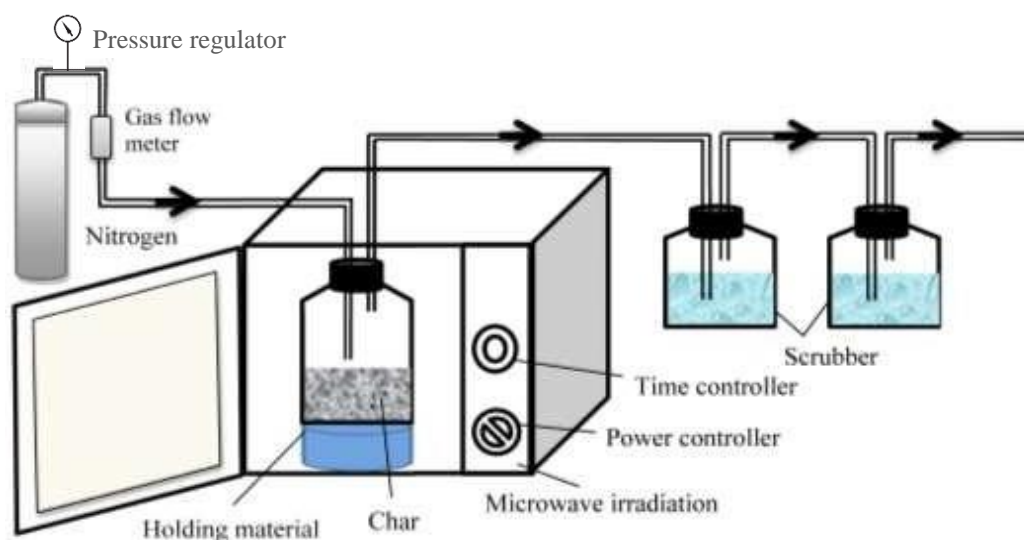
Figure (3.5): Schematic diagram of experimental setup for AC by electrical Microwave (Alslaibi et al., 2013a)

Different containers have been tested to determine the ability to stand inside the microwave with high temperature such as the ordinary flask, Pyrex flask, and clay dishes(Alslaibi et al., 2013b; Ashour, 2013), the results were broken flask or container after 15 min. The solution was found by using completely closed container from clay (To ensure a closed atmosphere and no nitrogen gas leakage) and inside it another container made of ceramic (Due to its tolerance to high temperatures) as shown in Figure (3.6)

Figure (3.6): The container used in activation process in microwave

The final arrangement of the electrical microwave as described above is illustrated in Figure (3.7).

Figure (3.7): Electrical microwave

The activation process of char was studied taking into account the change in the activation time factor (5-10-20-30-40 min). While, the impregnation ratio and activation power out of the scope of the present study and will be constant values based on results obtained from previous studies.

Chemical activation method using $ZnCl_2$ was used to activate the char. Samples of char were impregnated with a specific amount of $ZnCl_2$. $ZnCl_2$ amount used according to the specific IR of 1.6: 1 (Deng et al., 2009).

Then, distilled water was added to dissolve all $ZnCl_2$ pellets. The impregnation process was performed at room temperature for 24 hours, thus incorporating all chemicals into the inside of the molecules. After that, the $ZnCl_2$–impregnated char was activated by commercial microwave with a frequency of 2.45 GHZ at radiation power of 700W (Maximum power given by the user's microwave device) and different activation time (5-10-20-30-40) min under N_2 flow of (300-500 cm^3/min). after that, the samples were cooled while maintaining N_2 flow until room temperature 25 ^oC and then washed with distilled water, HCL and NaOH until pH was within range 6.5 to 7.5. Then, sample were dried in an oven at 105 ^oC for 24 hours. Finally, the resulted dried AC samples were kept and stored in a well-sealed glass jar until use. Figure (3.8) summarizes the steps of AC production by chemical activation via microwave heating.

Crushed olive stones was washed with distilled

Sieved to a desired particle size of 1.7-2.8

Carbonization at 700°C for one hour

Impregnation with specific amount of $ZnCl_2$

Activation of char by microwave at power 700 W and variance time (5-10-20-30-40) min

Washing with distilled water and HCL and NaOH (0.1 M) until pH 6.5-7.5
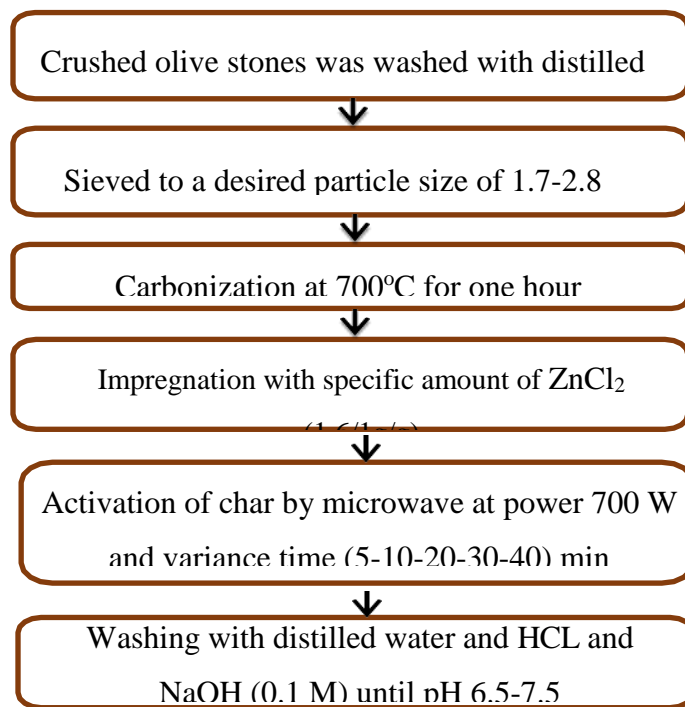
Figure (3.8): Procedure of AC preparation

3.3.2. Characterization of the prepared activated carbon

As explained in section 2.4.5, there are many important characteristics of prepared activated carbon (PAC), some of which can be measured by standard methods and the others by alternative rough methods, due to the lack of the Equipment necessary for standard methods in the Gaza strip.

3.3.2.1. Carbon yield

Three samples with known initial weight W_i from precursor were washed and dried at 105 °C for 24 hours. These samples were used to measure the yielding of carbonization. After the carbonization process completed, the sample were cooled to room temperature, and then the weight of the three sample W_f were determined by electronic balance and recorded for calculating the yield by using the following equation:

$$\%Y = \frac{w_f}{w_i} * 100 \%$$
(3.1)

3.3.2.2. Surface area

As explained in section 2.4.5, The Acetic acid method is used assuming a monolayer coverage, according to Langmuir isotherms. It is used because it is cheaper and can be done in the Gaza labs.

Firstly, acetic acid method was used to measure the surface area of a commercial activated carbon (CAC) with a known surface area measured by Brunauer- Emmett-Teller (BET) to test the completed procedure and to know the correction factor for the following measurements of surface area of the prepared activated carbon. The characteristics of CAC as described by the manufacturer (Jacobi Carbon - Aqua-Sorb 2000) are shown in Table (3.3).

Table (3.3): Characteristics of CAC (Jacobi Carbon – Aqua-Sorb 2000)

Parameter	Unit	Value	Test Method
Surface area	m^2/g	1100	BET N_2

Total pore volume	cm^3/g	1.04	Porosimetry(N$_2$/Hg)
Iodine number	mg/g	1050	ASTM D4607
Methylene blue	mg/g	280	JACOBI T4001
Apparent density	Kg/m^3	470	ASTM D2854
Bed density, backwashed and drained	Kg/ m^3	410	-
Moisture content -as packed	%	2	ASTM D2867
Water soluble matter	%	0.2	ASTM D5029
Wettability	%	99.5	JACOBI T4003
pH	-	8	ASTM D3838
Ball-pan hardness number	%	95	ASTM D3802
Chlorine half-length value (12x40 USS)	cm	2.2	DIN 19603

After completion of the activation process, the surface area of PAC is found using the acetic acid method as mentioned above in section 2.4.5. Then, the values are multiplied by the correction factor derived from the measuring of surface area of CAC by the BET N$_2$ and acetic acid method as shown in the following equation:

Surface area BET = Surface area acetic * correction factor   (3.2)

3.3.2.3.   Bulk density

As described in section 2.4.5-B for the standard procedure to measure the bulk density, three dried samples of 200 ml were taken on top of a vibration machine type (DRAGON LAB SK-330- Pro) with a frequency of 250 tab/min and the volume is weighted after 5 min (i.e. after 1250 tab/min), Repeat the procedure until no any change in volume is recorded, then by electronic balance (LAC.114 LARK) the samples are weighed and recorded. Then the Bulk density was calculated using the following equation:

Db = 1000 M/V   (3.3)

3.3.2.4. ash content

As explained in the section 2.4.5-C, three samples of PAC were dried in the oven at 105 ^{o}C for a few hours until reaching a constant weight. The three samples are then placed in a dry open crucible and placed in the muffle furnace at 650 ^{o}C for 1 hour and their weight are measured. The same step is repeated until there is no change in weight between the successive weights. The ash content calculated using the following equation

$$Ac = 100 \, (B\text{-}G) \, / \, (F\text{-}G) \tag{3.4}$$

Figure (3.9) shows the arrangement of the crucible and the furnace.

Figure (3.9): Muffle furnace for measuring ash content

3.3.3. Optimization of activated carbon

It is clear in the review of literature that there are many factors affecting activation such as radiation power, IR and activation time. In this research, we used a constant value for both the activation power and the IR of 700 W and 1.6/1 g/g, respectively (Deng et al., 2009). But the activation will be conducted at different times (5-10-20-30-40 min) to find optimum activation time which gives the best surface area. The process was conducted in triplicate to get consistent results. After that, the activation time that gives the highest surface area called (optimum activation time) and thus the optimum preparation conditions for AC will be adopted in all subsequent activation processes

3.3.4. Nitrate adsorption experiments

Nitrate adsorption onto AC surfaces was studied by batch adsorption experiments. For comparisons purposes, Batch adsorption experiments were conducted on prepared and commercial AC. Adsorption rate is affected by the nature of adsorbent and adsorbate and experimental conditions (temperature, initial pH, contact time, adsorbent dosage, and initial adsorbate concentration). The effect of the five factors on the removal of nitrates were investigated. In addition, the optimum conditions that achieve the highest rate of nitrate removal was determined.

3.3.4.1. Determination method of nitrate ion concentration

Nitrate ion concentration in all experiments in this study was determined by a standard method called "Ultraviolet Spectrophotometric Screening Method". This method followed exactly the procedure described in the Standard Methods for the Examination of Water and Wastewater (Clesceri, Greenberg, & Eaton, 1998). Nitrate concentration was measured on a CT-2200 spectrophotometer shown in Figure (3.10). A spectrophotometer is an instrument that measures the amount of the intensity of light absorbed after it passes through sample of nitrate solution. With the spectrophotometer, the amount of nitrate (concentrations) can also be determined by measuring the intensity of light detected. For nitrate ion, the maximum absorbance at wave length 220 nm was measured against the background of the redistilled water. The absorbance at 275 nm was measured to determine the interference with dissolved organic matter. Net absorbance due to nitrate was calculated by the following equation:

Absorbance due to nitrate = Abs $_{220}$ - [2 × Abs $_{275}$]   (3.5)

When the absorbance is more than one, proper dilution has been done and a conversion factor has been used in the calculation.

Percentage of nitrate removal defined as a ratio of the difference between initial and final nitrate concentration to the initial nitrate concentration as show in Equation:

$$Nitrate\ removal\ (\%) = \frac{C_o - C_e}{C_o} * 100$$ (3.6)

Where, C_o and C_e (mg/l) are sample concentrations at initial and at equilibrium, respectively.

Figure (3.10): Spectrophotometer

3.3.4.2.   Nitrate stock solution preparation

To conduct the batch study, synthetic solution (nitrate stock solution) was prepared by dissolving certain amount of Potassium Nitrate KNO_3 (1.63 g) which was pre-dried at 105 ºC for 24 hours in 1000 ml distilled water, and then the standard curve of the stock solution (shown in appendix B) was determined by plotting value of net absorbance vs. concentration of standard nitrate solution. After that, stock solution was diluted with distilled water to obtain the desired concentration (usually called work solution) by using dilution equation:

$$C_i \, V_I \; = \; C_f \, V_f \tag{3.7}$$

Where C_i (M) is the initial concentration or molarity, V_i (ml) is the initial volume, C_f (M) is the final concentration or molarity and V_f (ml) is the final volume.

3.3.4.3. Factors affecting adsorption

Batch adsorption was performed in 250 ml Erlenmeyer flasks where 100 ml of the solutions was used in each experiments. A specific amount of activated carbon, a known initial concentration of adsorbate, a known temperature and specific pH were used in each flask in experiments and kept in a digital shaker (DRAGON LAB SK-330-Pro) as shown in Figure (3.11). All experiments were conducted in triplicate to get consistent results. The removal percentage was calculated using the following equation

$$Nitrate\ removal\ (\%) = \frac{Cf - Ce}{Ce} * 100 \tag{3.8}$$

Were C_f (mg/l) calculated by using the equation: $Cf = \frac{abs. - 0.0124}{0.0493}$ \qquad (3.9)

Figure (3.11): Digital shaker (DRAGON LAB SK-330-Pro)

A. Effect of pH

In this section, the effect of pH on adsorption of nitrate using PAC and CAC was investigated in the range $2 - 8$. The initial solution pH was varied as desired by using $0.1M$ solution of NaOH or HCL. Measurements of pH was performed on ADWA KFT AD11 pH meter. Nitrate solution (100 ml, 70 mg/l) was added to 1 g of AC in 250 ml Erlenmeyer

flasks. The mixture was then shaken by a digital shaker at 250 rpm at room temperature 25 °C for 1 hour. After that, the samples were filtered through a 0.45 μm pore size filter paper and the concentration of nitrate (C_f) was determined.

B. Effect of contact time

Contact time is an important parameter affect rate of adsorption of adsorbate molecules. Nitrate adsorption was tested in relation to different values of contact time of 30, 60, 90, 120, 150, 300 min in the presence of CAC and PAC.   Adsorbent dosage, pH and initial concentration were 1 g, 4 and 70 mg/l, respectively. Volume of Nitrate solution was 100 ml placed in 250 ml Erlenmeyer flasks. The mixture was then shaken by a digital shaker at 250 rpm at room temperature 25 °C. After that, the samples were filtered through a 0.45 μm pore size filter paper and then percent of nitrate removal was determined.

C. Effect of adsorbent dosage

Nitrate adsorption was tested in relation to amount of adsorbents (whether CAC or PAC). In this study, the amount of adsorbent used were 0.5, 1, 1.5, 2 and 3 g. Contact time, pH and initial concentration were 100 min, 4 and 70 mg/l, respectively. Volume of Nitrate solution was 100 ml placed in 250 ml Erlenmeyer flasks. The mixture was then shaken by a digital shaker of 250 rpm at room temperature 25 °C. after that, the samples were filtered through a 0.45 μm pore size filter paper and the concentration of nitrate C_f was determined. Then, the percent of nitrate removal was calculated.

D. Effect of adsorbate initial concentration

Effect of initial concentration of adsorbate on adsorption study in the presence of CAC and PAC was investigated. Nitrate adsorption was tested in relation to different values of initial concentration of 20, 40, 80, 100 and 120 ppm. pH, Contact time and adsorbent dosage were 4, 100 min, and 2 g, respectively. Volume of Nitrate solution was 100 ml

placed in 250 ml Erlenmeyer flasks. The mixture was then shaken by a digital shaker of 250 rpm at room temperature 25 o C. after that, the samples were filtered through a 0.45 μm pore size filter paper and the concentration of nitrate C_f was determined. Then, the percent of nitrate removal was calculated.

E. Effect of temperature

Nitrate adsorption was tested in relation to different values of temperature of 10, 20, 30, 40 and 50 ℃ by using shaker water bath (YCW-012) shown in Figure (3.12). 100 ml of Nitrate solution with pH 4 was placed on 2 g adsorbent in 250 ml Erlenmeyer flasks. The mixture was then shaken by a digital shaker of 250 rpm for 1 hour. After that, the samples were filtered through a 0.45 μm pore size filter paper, and then, the percent of nitrate removal was calculated at different temperatures.
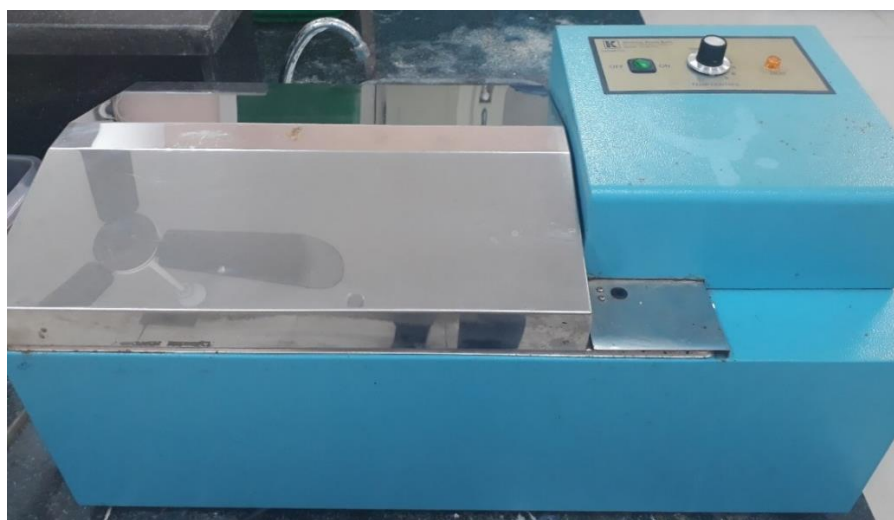
Figure (3.12): Shaker water bath

3.3.4.4. Adsorption isotherm models

Adsorption isotherms, also known as equilibrium data, is achieved when the capacity of the adsorbent materials is reached. In this study, equilibrium isotherms were studied and described using Langmuir and the Freundlich isotherms. Volume of nitrate solution was

fixed at 100 ml, but dosage of the adsorbent media was varied. Optimum pH, contact time, initial concentration and temperature were fixed based on results in section 4.4.1.

Concentration of nitrate in solution was determined before and after shaking. Adsorbate adsorbed (x) and adsorbent mass (m) and ratio (x/m) was determined. In Freundlich model, isotherm parameters (k_f and n) were determined by plotting logarithm of (x/m) against logarithm of C. While in Langmuir model, isotherm parameters (Q & b) were determined by plotting $(x/m)^{-1}$ against 1/C. Applicability and suitability of isotherm equation to equilibrium data was compared by judging values of coefficient of determinations, R^2. Langmuir and Freundlich can be calculated using the equations as described previously in section 2.3.4.1 and 2.3.4.2

3.3.4.5.   Kinetics studies

Generally, Adsorption mechanism and potential rate-controlling processes was investigated by using Kinetic modeling. In this study, the kinetics of nitrate adsorption on PAC and CAC were studied under optimal conditions through the pseudo-first order, the pseudo-second order and intra-particle diffusion models as the following equations. The principles of kinetic models have already been explained in section 2.3.5. Adsorption kinetics experiments were performed by mixing 100 ml of nitrate solution with AC at different contact times. The optimum pH, dosage of adsorbent, initial concentration and temperature were determined based on the results in section 4.4.1.

The results of kinetic models were determined by using the equations that described previously in section 2.3.5.

Chapter 4

Results and discussions

Chapter 4
Results and discussions

4.1. Introduction

This chapter presents experimental results of current study. Initially, provides characteristics of produced char and AC such as carbon yield, surface area, bulk density and ash content. Optimization of OSAC preparation factors based on the results of surface area are also included. Effects of factors (dosage, pH, contact time, temperature and initial concentration) on removing nitrate are discussed and the optimum removal efficiency of nitrate were presented. Adsorption isotherm models using Freundlich and Langmuir models were plotted and discussed. Adsorption kinetics results were also presented.

4.2. Characteristics of char (after carbonization)

4.2.1. Yield of char

Three samples with initial weight $W_i = 400$ g from Precursor (crushed olive stones) were used to measure the carbon yield. The samples were cooled to room temperature after carbonization process was finished. The final weight W_f of the same samples were weighted. The results were 115, 113.6 and 110.4 g. the carbon yield after carbonization was calculated by using the equation:

$$\%Y = \frac{W_f}{W_i} * 100 \%$$ (4.1)

The results were 28.75, 28.4 and 27.6 %, and the average of the yield percentage of char was 28.25 %. Comparative results were noted by Martinez et al. (2006), they reported that the carbon yield of AC prepared from OS was 25.15%. Also, Ashour (2013) measured the

carbon yield after carbonization of OS and the result was 23.9%. While Kula, Uğurlu, Karaoğlu, and Celik (2008) reported that the carbon yield of OSAC was 40% .

4.3. Characteristics of activated carbon (after activation)

4.3.1. Yield of activated carbon

As measured in section 4.2.2, the carbon yield after carbonization was 28.25%. Three samples of this char with weight W_i 30 g has been considered in measuring the yield of PAC by activation with microwave radiation for 30 min and assessed by $ZnCl_2$ 1.6/1 g/g. After activation, the three samples were washed with distilled water and dried in the oven at 105 ^{o}C for 24 hours, then the weights of three samples W_f were 25.4, 25.6, 26.1 g. The carbon yield after activation was calculated using the equation:

$$\%Y = \frac{W_f}{W_i} * 100 \text{ \%} \tag{4.2}$$

The results were 84.67, 85.33 and 87 %, and the average of the yield percentage was 85.67 %. The total yield of PAC form OS at optimum activation time (30 min) is equal 0.8567*28.25% = 24.2%

Ashour (2013) studied the preparation of AC from OS under microwave radiation by using chemical agent KOH with IR 2:1 g/g, he found that the optimum activation time and the total yield are 20 min and 20.02%, respectively.

4.3.2. Surface area

The surface area of CAC and PAC were determined by using the acetic acid method, because it can be done in Gaza labs.

4.3.3.1. Commercial activated carbon

The resulting isotherm of surface area of CAC shown in the Figure (4.1).
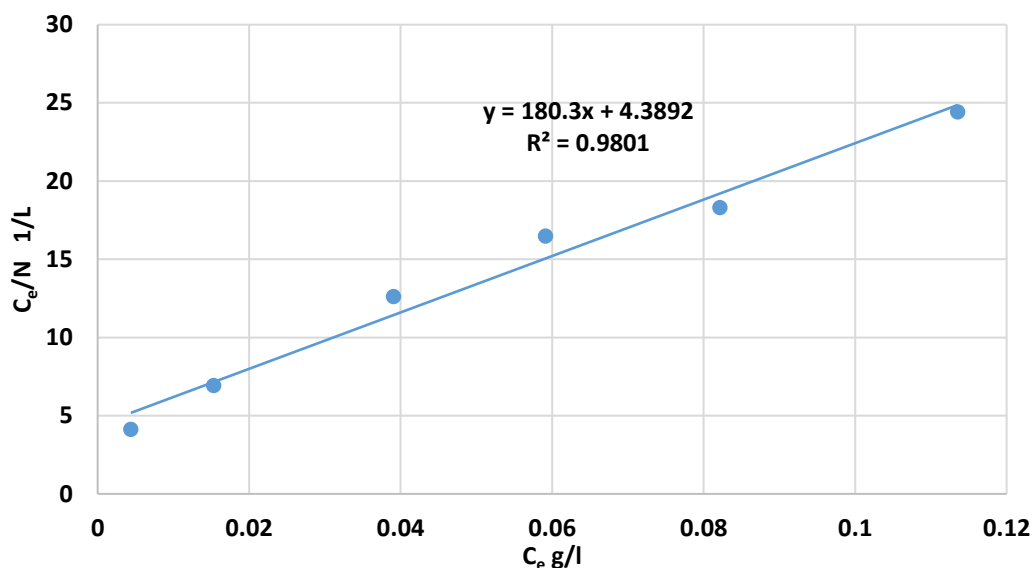
Figure (4.1): Surface area of CAC by acetic acid method

The measured surface area of CAC is 725.6 m²/g (as shown in Appendix A), while the BET surface area as measured by the manufacture is 1100 m²/g. therefore, the correction factor of 1.52 was considered to find out the BET surface area of the PAC as shown later.

4.3.3.2. Prepared activated carbon

Surface area of prepared activated carbon were calculated by using acetic acid isotherms at several activation time (5,10,20,30 and 40 min). Each experiment was conducted in triplicate to get consistent results. It is observed that the surface area of AC increases with an increase in the activation time in the range of 5-30 min, and then begins to decrease after the activation time 30 min. This may be due to the destruction of small pores due to exposure to a long period of microwave radiation (K. Foo & Hameed, 2012b). Figure (4.2) describes clearly the change of surface area of PAC by increasing activation time. the calculations are included in Appendix A.
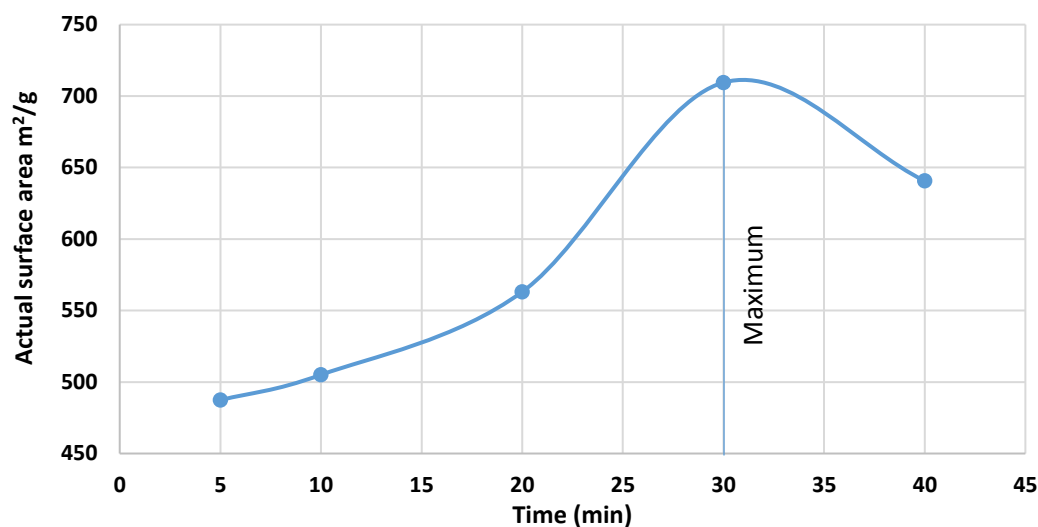
Figure (4.2): Activation time vs. surface area

Also, its noted that when the activation time was increased from lower activation time (5 min) to 20 min, there was a low increasing rate in the surface about 80 m^2/g. While when the activation time was increased from 20 to 30 min there was an increase in the surface area by about 140 m^2/g. But after 30 min, the surface area began to decrease.

In current study, it is observed that the optimal activation time was high (30 min) compared to the results of previous studies which showed that it ranged from (5-10 min). This may be due to the container used in the activation process inside the microwave. It is made of clay and inside it another container made of ceramic as previously shown in Figure (3.6). Thus, a large part of the heat produced by microwave may have been absorbed by the container. Therefore, there was a need to increase the activation time to reach the optimal activation time.

A 30 min activation time is considered as the optimum activation time. So, all the quantity of char has been activated based on this time.

4.3.3. Bulk density

The results of measuring the bulk density for the three samples are as shown in the Table (4.1).

Table (4.1): Bulk density calculation

Sample No.	Volume (ml)	Sample weight (g)	Bulk density (kg/ m³)
1	200	86.4	432
2	200	87.6	438
3	200	85.9	429.5
Average of bulk density			**433.2**

Close results were recorded by Ashour (2013) when he used activated carbon prepared from olive stones to remove detergents. He reported that the Bulk density is 444.67 kg/m³.

4.3.4. Ash content

Three sample with initial weight of 3 g of AC were placed in the muffle furnace at 650 °C. Table (4.2) shows the calculation of ash content.

Table (4.2): Ash content calculation

Sample No.	Sample weight (g)	Weight of ash (g)	Ash content (%)
1	3	0.069	2.3
2	3	0.063	2.1
3	3	0.078	2.6
Average Ash content			**2.33**

It observed that the ash content is low compared to other studies such as (El-Hamouz et al., 2007) where the ash content is 6%, this could be referred to the low content of residual minerals in the stones (El-Sheikh, Newman, Al-Daffaee, Phull, & Cresswell, 2004), in addition to multiple cleaning of the olive stones at the preliminary stages of sample collections and pretreatment. This indicates that the efficiency and adsorption capacity of the PAC will be increased, due to the decrees of ash content.

4.4. Nitrate adsorption

Nitrate adsorption onto AC surfaces was studied by batch adsorption experiments. For comparisons purposes, Batch adsorption experiments were conducted on both prepared

and commercial AC. As explained in section 3.3.4.3, there are many factors affecting the adsorption process which investigated in the current study such as pH, dosage, contact time, initial concentration and temperature. In addition, the optimum conditions that achieve the highest rate of nitrate removal were determined. Also, adsorption isotherms and kinetics model were used to obtain the best fit of the adsorption isotherm and kinetic data.

4.4.1. Factors affecting adsorption

More calculations in this section are included in Appendix B

4.4.1.1. Effect of pH

The effect of pH on adsorption of nitrate from aqueous solution using PAC and CAC as adsorbent was investigated in the range 2 – 8. The initial solution pH was varied as desired by using 0.1M solution of NaOH or HCL. Nitrate solution (100 ml, 70 mg/l) was added to 2 g of AC in 250 ml Erlenmeyer flasks. The mixture then was shaken by a digital shaker of 250 rpm at room temperature of 25 ºC for 1 hour. The effect of initial pH on the removal of nitrate is shown in Figure (4.3).
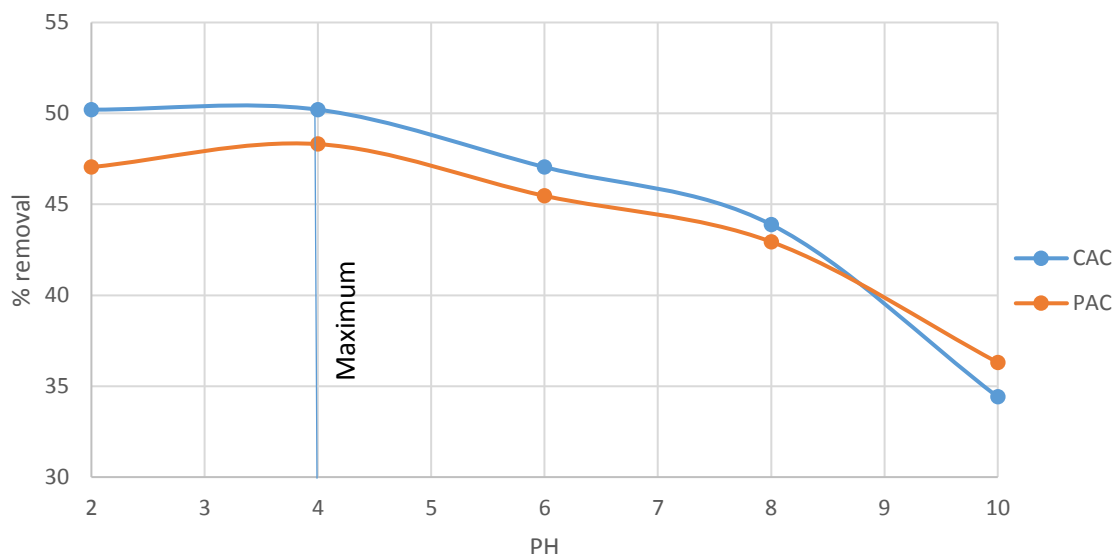
Figure (4.3): Effect of solution pH on nitrate ion removal by PAC and CAC

Generally, it is observed that the percentage of nitrate removal decreased with increase in solution pH from pH 2 to pH 10. The decrease of adsorption at high pH can be referred to the increase of the hydroxide ions, which are adsorbed quit strongly compared to other ions available in the solute like nitrate ions, in addition water solubility is expected to increase with increasing polarity, this will result adsorption decreases as polarity increases (Weber, 1974). The highest nitrate removal on PAC and CAC of 48.3 and 50.2 % were achieved around pH 4. This is due to electrostatic attraction between nitrate and the positively charged surface site on the AC (Zyoud et al., 2015). Consequently, initial solution pH was set at 4 for all subsequent experiments.

4.4.1.2. Effect of contact time

Nitrate adsorption on PAC and CAC was tested in relation to different values of contact time of (30, 60, 90, 120, 150, 300 min). Figure (4.4) shows the effect of contact time on nitrate ion removal.

Adsorbent dosage, pH and initial concentration were 2 g, 4 and 70 mg/l, respectively. volume of Nitrate solution was 100 ml placed in 250 ml Erlenmeyer flasks. The mixture was then shaken by a digital shaker of 250 rpm at room temperature 25 °C.
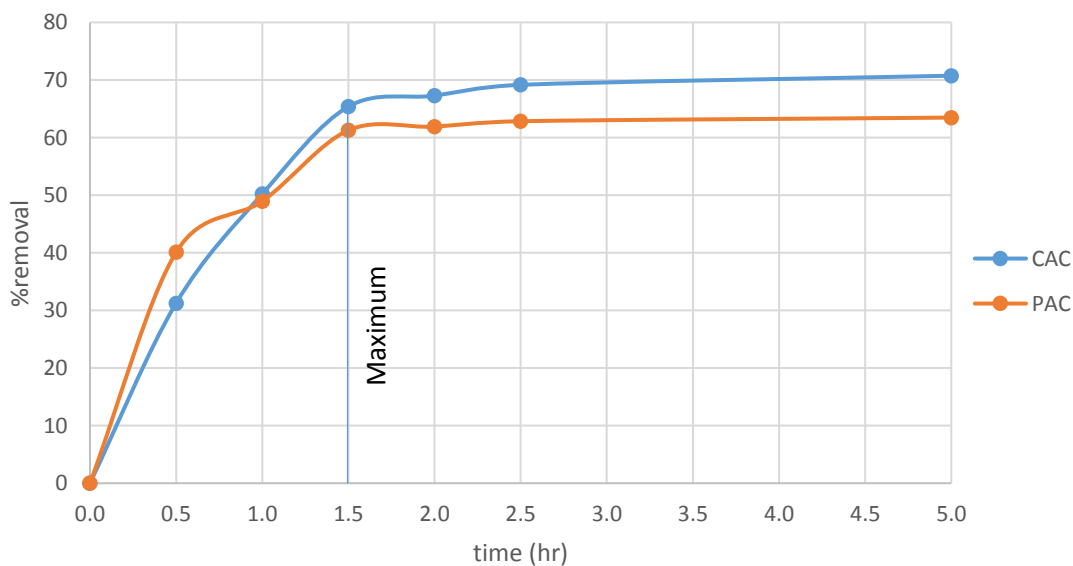
Figure (4.4): Effect of contact time on nitrate ion removal by PAC and CAC

It is observed that the percentage of nitrate removal on PAC and CAC increased with increase in the time of contact. This is due to longer contact between solid and liquid, that allow better interaction between media and adsorbate (Foul et al., 2009). The percentage of removal at time 30 min was 40.1% and 31.3% of PAC and CAC, respectively. while at time 90 min the percentage was 61.2 % and 65.4 %, respectively. After that the removal rate remained constant, where no more nitrate was removed from the solution. This is due to the decresed number of active sites on adsorbent surface (Al-Anber, 2011).

Initially, the rapid adsorption of nitrate in the initial stage was due to the availability of a large number of active sites on the adsorbent surface. At longer time, it was difficult to occupy the remaining sites because of the repulsive forces between solute molecules on solid and bulk phases (Hameed & El-Khaiary, 2008). Consequently, PAC and CAC contact time was set at 90 min for all subsequent experiments.

4.4.1.3. Effect of adsorbent dosage

Removal results of nitrate ion from solution using PAC and CAC are shown in Figure (4.5). the amount of adsorbent used were 0.5, 1, 1.5, 2 and 3 g. Remaining variables of process, i.e. pH, contact time, and initial concentration of adsorbate were fixed at 4, 90 min and 70 ppm, respectively.
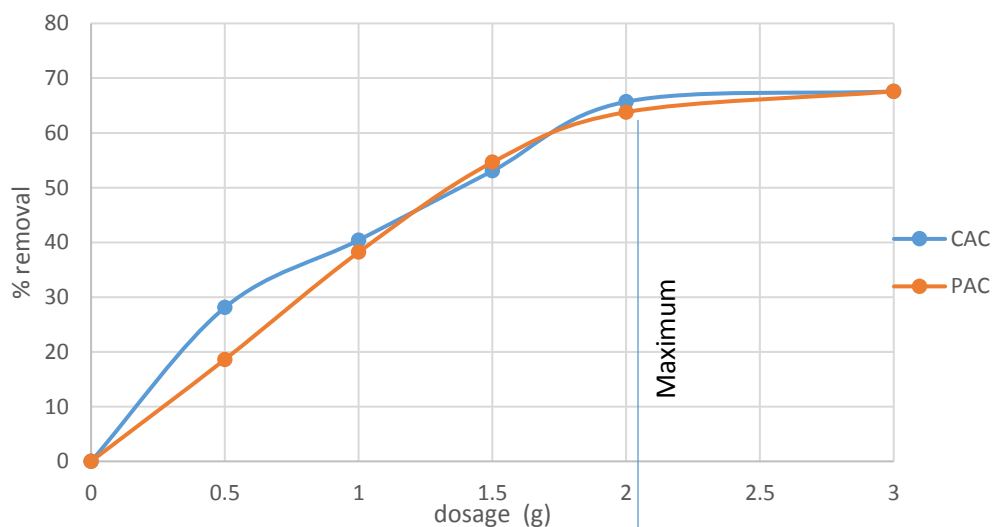
Figure (4.5): Effect of adsorbent dosage on nitrate ion removal by PAC and CAC

It is observed that percent of nitrate removal was proportional to dosage of PAC and CAC till 2 g level, after which it has been observed that only a small removal occurred. This can be explained by the fact that higher dose of adsorbent, the greater contact surface offered to the adsorption, i.e. more active sites are available (Al-Anber, 2011).

Best percent of nitrate removal on PAC and CAC was 63.8% and 65.7% using 2 g of adsorbent. So, adsorbent dosage of 2 g was used for all subsequent experiments.

4.4.1.4. Effect of initial concentration

Effect of initial concentration of nitrate on percentage of nitrate ion removal from solution using PAC and CAC are shown in Figure (4.6). Initial concentration of nitrate diverged from 20 to 120 mg/l (ppm). Remaining variables of process, i.e. pH, contact time, and dosage of adsorbent were fixed at 4, 90 min and 2 g, respectively.
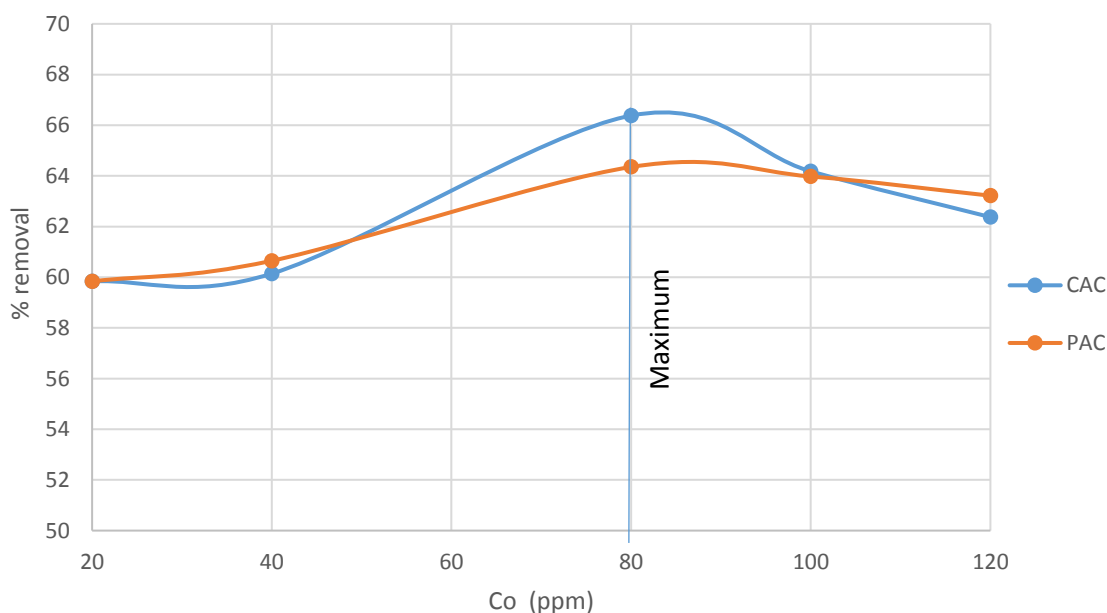
Figure (4.6): Effect of initial concentration on nitrate ion removal by PAC and CAC

It is observed that percent of nitrate removal increase with increase of initial concentration till 80 mg/l, after which it decreased. However, the increase in the removal ratio of nitrate was not significant. As the initial concentration increased from 20 to 80 mg/l, the increase

in nitrate removal was from 60% to 64%, which represents only 4%. Therefore, it can be said that the effect of the initial concentration on percentage of nitrate removal is very low and unimportant. Best percent of nitrate removal on PAC and CAC was 64.4% and 66.4% with 80 mg/l initial concentration of nitrate in solution.

4.4.1.5. Effect of temperature

Figure (4.7) shows effect of temperature on percentage of nitrate ion removal from solution using PAC and CAC. Temperature diverged from 10 to 50 ºC by using shaker water bath. Remaining variables of process, i.e. pH, contact time, dosage of adsorbent and initial concentration were fixed at 4, 90 min, 2 g and 80 mg/l, respectively. It is observed from the graph that the changing in removal percent of nitrate is not significantly, and this behavior adds to the advantages of adsorbents. Thus, the adsorbent can be used in treatment under various temperatures without affecting the adsorbent efficiency.
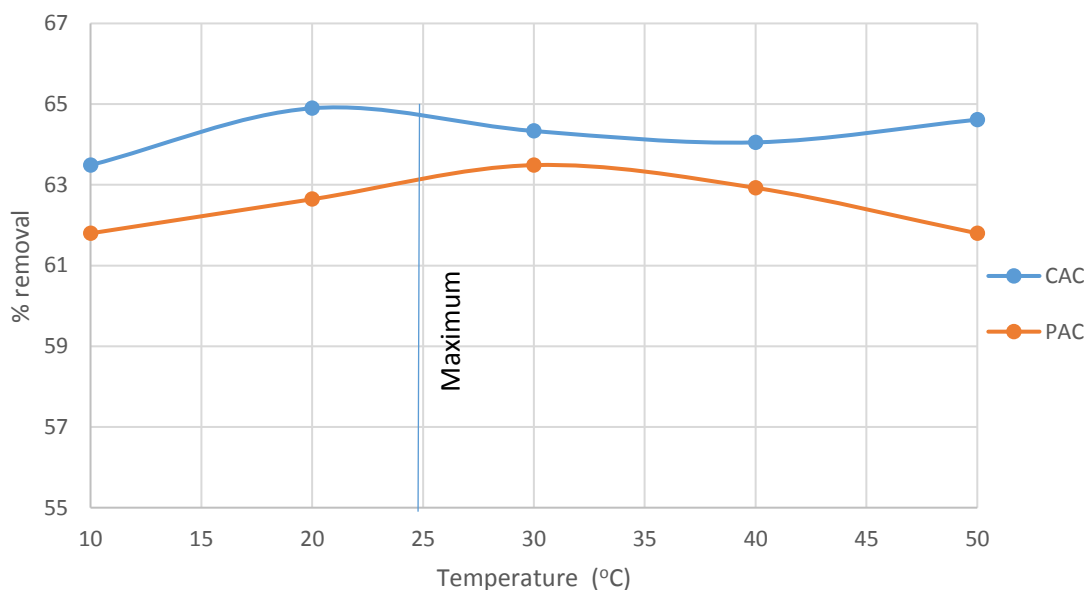
Figure (4.7): Effect of temperature on nitrate ion removal by PAC and CAC

4.4.2. Adsorption isotherm model

A. Adsorption isotherm model for PAC

The fitting of adsorption data, to Langmuir and Freundlich isotherm equations was investigated by plotting 1/C versus 1/(x/m) and log C versus log (x/m) which are presented in Figure (4.8) and Figure (4.9) for PAC, respectively. Table (4.3) list values of adopted constants and R^2 values of both Langmuir and Freundlich model, respectively.

In Langmuir model, RL value for nitrate adsorption on PAC were between 0 and 1 indicating that adsorption is a favorable process. It showed that R^2 value was relatively high (close to unity). Freundlich model also showed a high value of R^2. Öztürk and Bektaş (2004) stated that 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. Table (4.3) showed the value of (1/n) was 0.4935, therefor (n) value was 2.02 which considered smaller value that implies weaker interaction between the adsorbent and the adsorbate.

Based on the above, we can state that Langmuir model yielded the best fit of adsorption process. This means that nitrate adsorption occurs by monolayer adsorption on a homogenous surface without interaction between adsorbed molecules. The adsorption capacity (Q) value of nitrate using PAC was 5.76 mg/g.
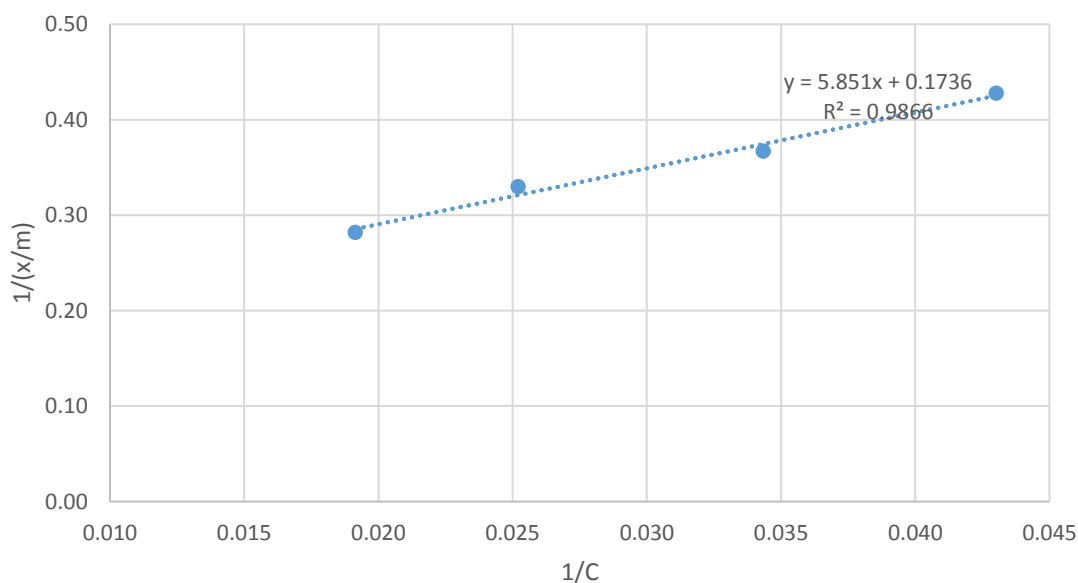
Figure (4.8): Langmuir isotherm model for nitrate adsorption on PAC
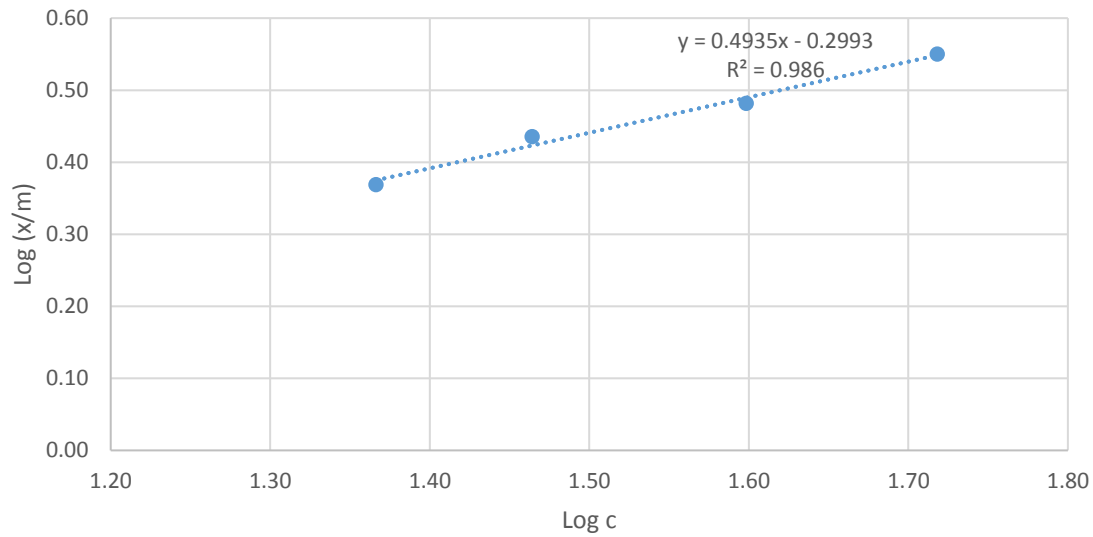
Figure (4.9): Freundlich isotherm model for nitrate adsorption on PAC

Table (4.3): Langmuir and Freundlich isotherm model parameters and correlation coefficient of nitrate adsorption onto PAC

Langmuir Isotherm Coefficients				Freundlich Isotherm Coefficients		
Q (mg/g)	b (L/mg)	R^2	RL	K $(mg/g)(L/mg)^{1/n}$	1/n	R^2
5.76	0.030	0.9866	0.3250	0.50	0.4935	0.9860
			0<RL<1		0<1/n<1	

Langmuir and Freundlich equations of PAC for nitrate can be written as shown in following equation:

$$\frac{x}{m} = \frac{0.1728C}{1+0.03C} \tag{4.3}$$

$$\frac{x}{m} = 0.5C^{0.4935} \tag{4.4}$$

B. Adsorption isotherm model for CAC

The fitting of adsorption data, to Langmuir and Freundlich isotherm equations was presented in Figure (4.10) and Figure (4.11) for CAC, respectively. Table (4.4) list values of adopted constants and R^2 values of both Langmuir and Freundlich model, respectively.

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Freundlich model also showed a high value of R^2. So, we can state that Freundlich model yielded the best fit of adsorption process. This means that nitrate adsorption occurs by multilayer adsorption on a heterogeneous surface. It represents the initial surface adsorption followed by the condensation effect that result from strong interaction between adsorbent and adsorbate. The adsorption capacity (Q) value of nitrate using CAC was 6.62 mg/g.

Table (4.4): Langmuir and Freundlich isotherm model parameters and correlation coefficient of nitrate adsorption onto CAC

Langmuir Isotherm Coefficients				Freundlich Isotherm Coefficients		
Q (mg/g)	b (L/mg)	R^2	RL	K $(mg/g)(L/mg)^{1/n}$	1/n	R^2
12.66	0.010	0.829	0.5892	6.62	0.8681	0.84
			0<RL<1		0<1/n<1	
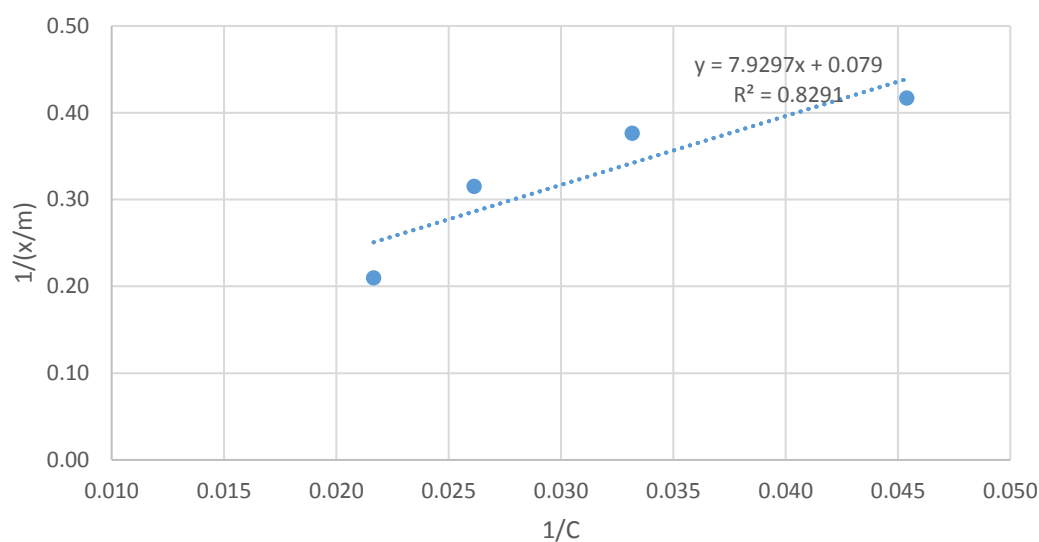
Figure (4.10): Langmuir isotherm model for nitrate adsorption on CAC
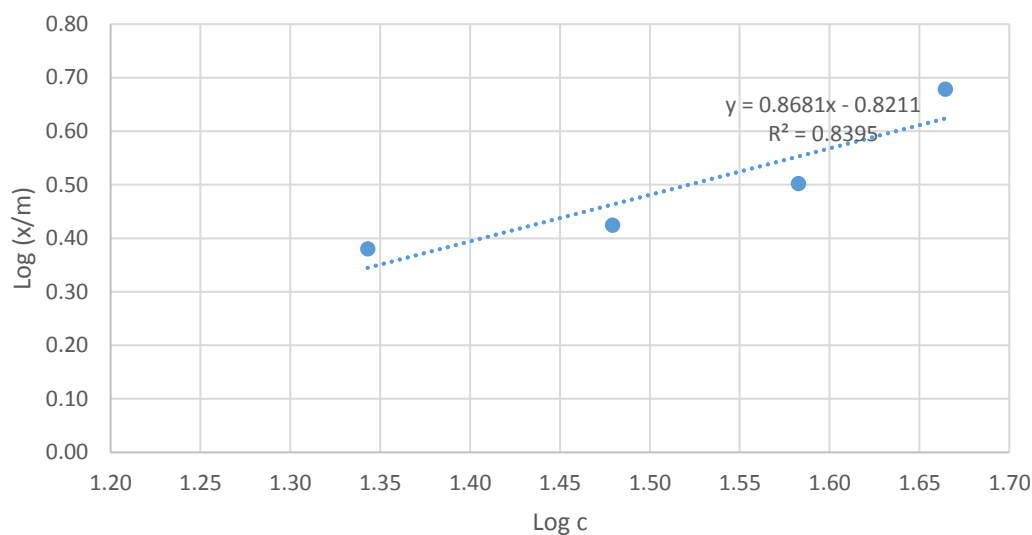
Figure (4.11): Freundlich isotherm model for nitrate adsorption on CAC

Langmuir and Freundlich equations of PAC for nitrate can be written as shown in following equation:

$$\frac{x}{m} = \frac{0.1266C}{1+0.01C} \tag{4.5}$$

$$\frac{x}{m} = 0.5C^{0.8681} \tag{4.6}$$

Appendix C shows experimental data of isotherm models using PAC and CAC for nitrate removal. Comparison of nitrate adsorption capacity on this adsorbent with other reported materials used for nitrate adsorption was given in Table (4.5).

Table (4.5): Comparison of nitrate adsorption capacity by different materials

Material	Mono layer capacity of the adsorbent (mg/g)	References
Coconut activated by $ZnCl_2$	10.3	(Namasivayam & Sangeetha, 2005)
Coconut activated by $ZnCl_2$	10.2	(Bhatnagar et al., 2008)
Sugar beet bagasse	9.14	(Demiral & Gündüzoğlu, 2010)

Commercial activated carbon	6.62	Current study
Activated red mud	5.85	(Cengeloglu, Tor, Ersoz, & Arslan, 2006)
Olive stone activated carbon	5.76	Current study
Olive stones activated by ZnCl$_2$	5.53	(Zyoud et al., 2015)
Coconut	1.72	(Namasivayam & Sangeetha, 2005)
Mustard straw charcoal	1.30	(Mishra & Patel, 2009)
Bamboo powder charcoal	1.25	(Öztürk & Bektaş, 2004)
CAC; retail outlet of Eureka Frobes Limitted Aquaquard	1.22	(Mishra & Patel, 2009)
Wheat straw charcoal	1.10	(Mishra & Patel, 2009)
CAC; Nacalai tesque Model 079-39, Jaban	1.09	(Öztürk & Bektaş, 2004)

It is observed that the adsorption capacity of the activated carbon prepared in the current study was within the range of different material used in other previous studies which was from (1-10 mg/g). This indicates that the activated carbon prepared from the olive stones using microwave heating showed a good adsorption capacity compared to the capacity throw carbon prepared from other materials in the removal of nitrates.

4.4.3. Adsorption kinetics model

Generally, Adsorption mechanism and potential rate-controlling processes was investigated by using Kinetic modeling for both PAC & CAC. This was done by using most common models of adsorption kinetics, namely, pseudo-first order, pseudo-second-order models and intra-particle diffusion models. Adsorption kinetics basic theory was discussed in Section 2.3.5.

Figure (4.12), (4.13) and (4.14) show pseudo-first-order, pseudo-second-order and intra-particle diffusion models of linear plots for nitrate on both PAC. Table (4.6) summarizes kinetic study results of nitrate adsorption onto PAC. Further calculations are included in Appendix C
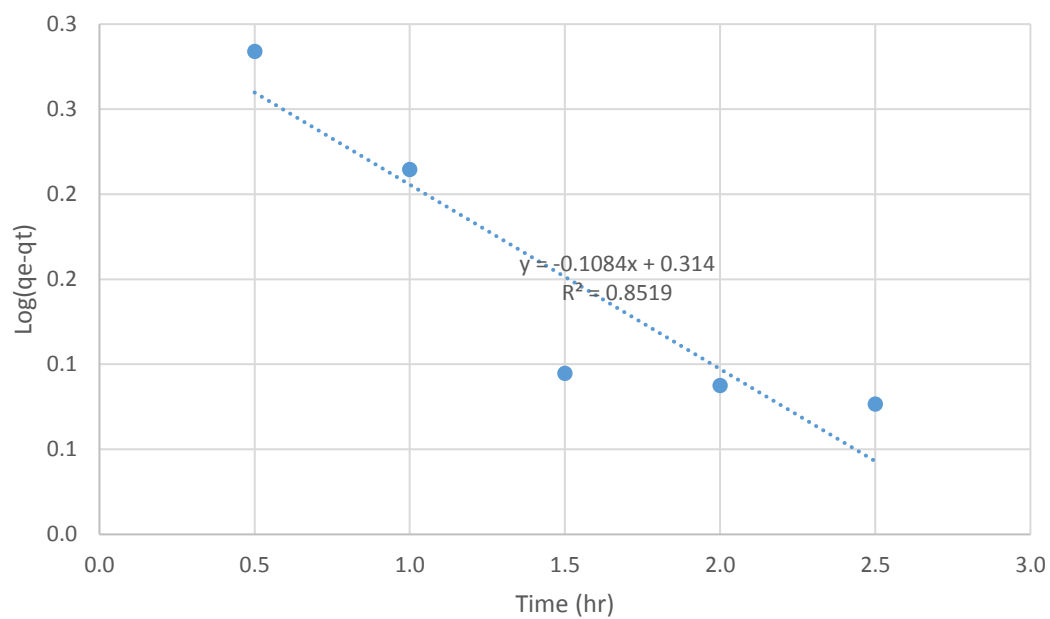
Figure (4.12): Pseudo-first order kinetic model of nitrate adsorption onto PAC
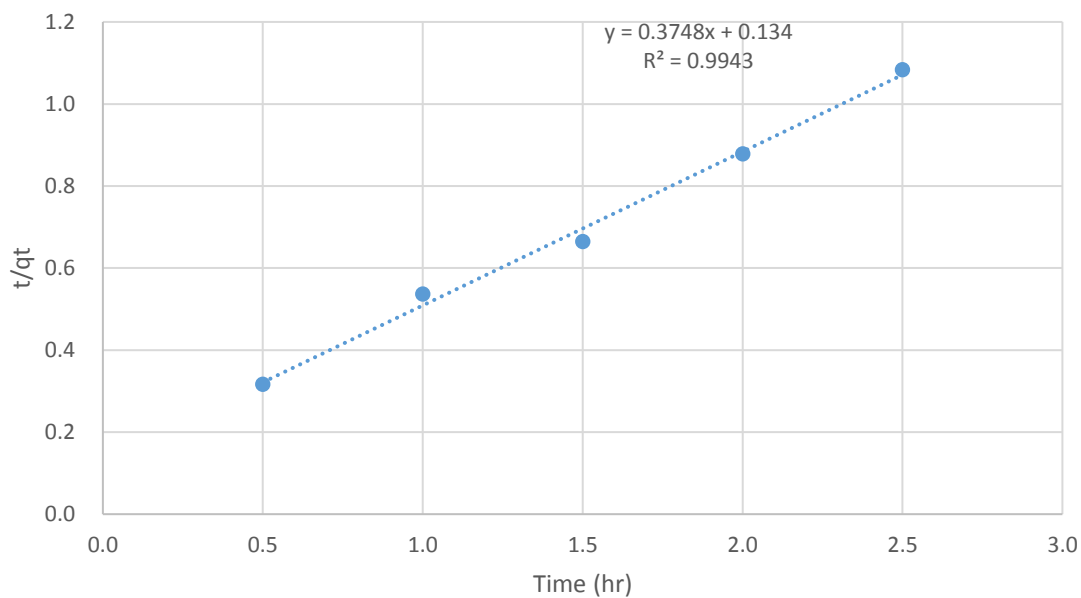
Figure (4.13): Pseudo-second order kinetic model of nitrate adsorption onto PAC
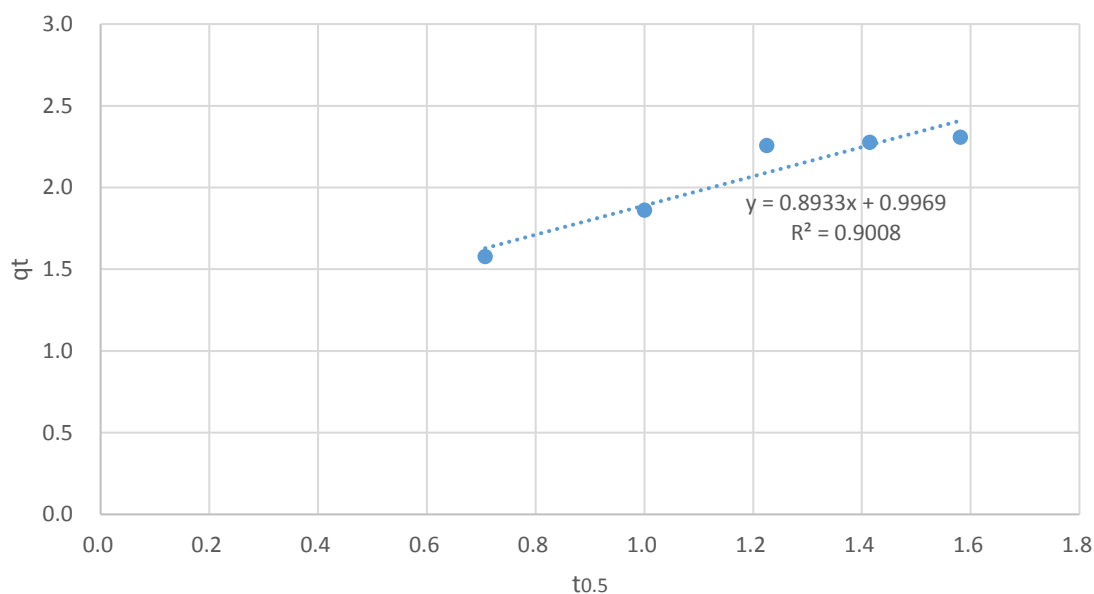
Figure (4.14): Intra-particle diffusion kinetic model of nitrate adsorption onto PAC

Table (4.6): Kinetic parameters for nitrate adsorption onto PAC

$q_{e, exp}$ (mg/g)	Pseudo-First Order Model			Pseudo-Second Order Model			Intra-Particle Diffusion	
	K_1 (h-1)	$q_{e, cal}$ (mg/g)	R^2	K_2 (g/mg h)	$q_{e, cal}$ (mg/g)	R^2	K_{id} (min-1)	R^2
2.257	0.250	2.061	0.852	1.048	2.668	0.994	0.893	0.901

Table (4.6) include R^2 value of pseudo-second order model is approaching unity. Also, it's results show better agreement with experimental data compared to intra-particle model. Therefore, it is safe to infer that nitrate adsorption systems on PAC followed pseudo-second order kinetic model. This mean that adsorption occur due to chemisorption- type mechanism (Krishni et al., 2014)

Figure (4.15), (4.16) and (4.17) show pseudo-first-order, pseudo-second-order and intra-particle diffusion models of linear plots for nitrate on both CAC. Table (4.7) summarizes kinetic study results of nitrate adsorption onto PAC. Further calculations are included in Appendix C
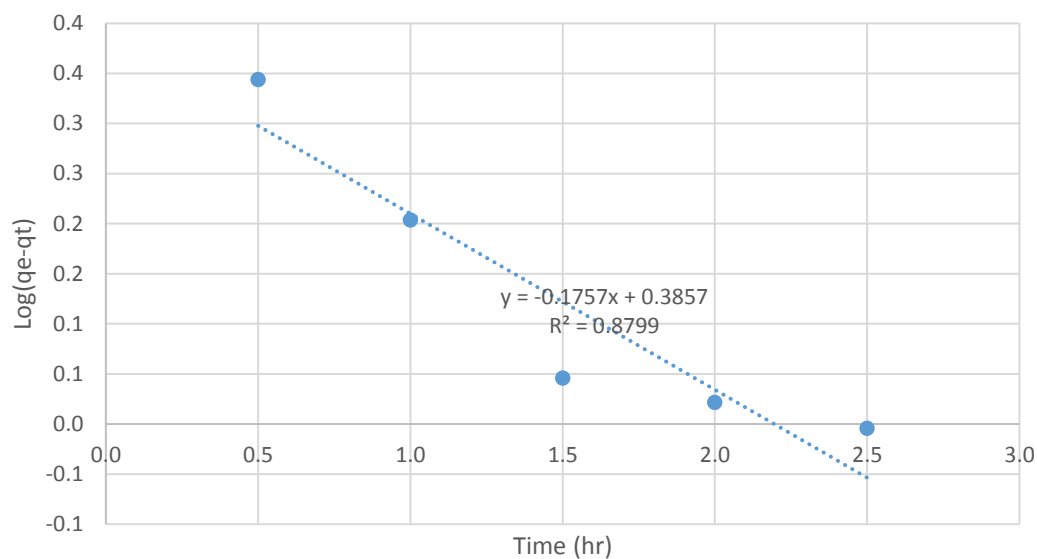
Figure (4.15): Pseudo-first order kinetic model of nitrate adsorption onto CAC
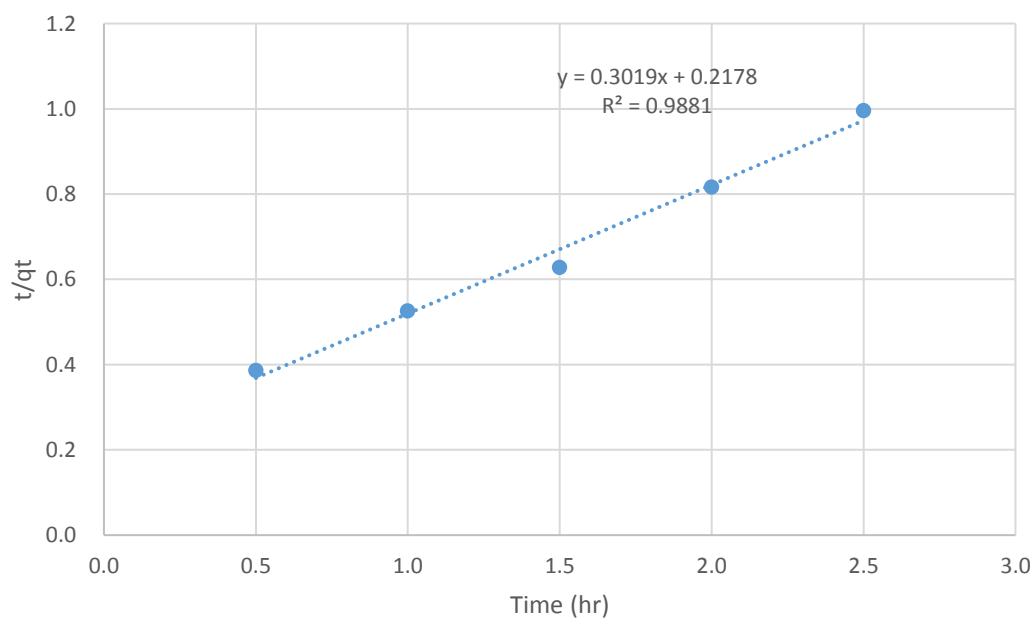
Figure (4.16): Pseudo-second order kinetic model of nitrate adsorption onto CAC
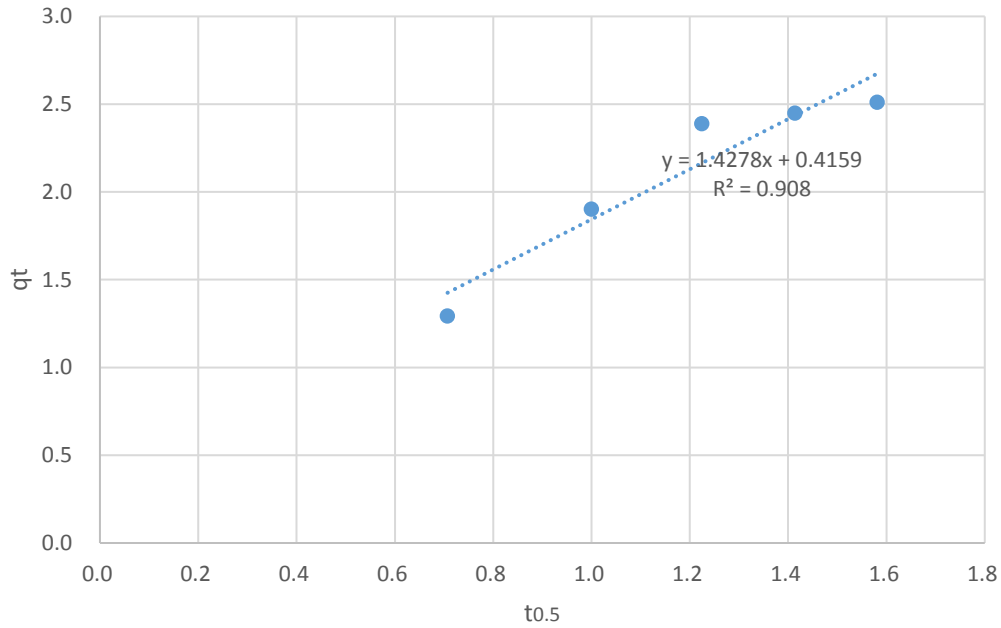
Figure (4.17): Intra-particle diffusion kinetic model of nitrate adsorption onto CAC

Table (4.7): Kinetic parameters for nitrate adsorption onto PAC

$q_{e, exp}$ (mg/g)	Pseudo-First Order Model			Pseudo-Second Order Model			Intra-Particle Diffusion	
	K_1 (h-1)	$q_{e, cal}$ (mg/g)	R^2	K_2 (g/mg h)	$q_{e, cal}$ (mg/g)	R^2	K_{id} (min-1)	R^2
2.388	0.405	2.431	0.879	0.418	3.312	0.988	1.428	0.908

Table (4.7) include R^2 value of pseudo-second order model is approaching unity. Also, it's results show better agreement with experimental data compared to other model. Therefore, it is safe to infer that nitrate adsorption systems on CAC followed pseudo-second order kinetic model. This mean that adsorption occur due to chemisorption- type mechanism (Krishni et al., 2014).

Comparison between PAC & CAC used in this research as adsorbent for nitrate was given in Table (4.8).

Table (4.8): Kinetic parameters for nitrate adsorption onto PAC

	PAC	CAC
Optimum conditions	The optimum conditions was achieved at time 90 min, pH 4, 2 g dosage, 80 mg/L initial concentrate and 25 $^{\circ}$C temperature.	
Isotherm model	Langmuir model (monolayer)	Freundlich model (multilayer)
Adsorption capacity mg/g	5.76	6.62
Kinetics model	Pseudo-second order (chemisorption mechanism)	

Chapter 5
Conclusion and
recommendations

Chapter 5

Conclusion and recommendations

5.1. Conclusion

5.1.1. Conclusion regarding activated carbon production

It can be concluded from the research that:

- AC was produced from OS under a carbonization temperature of 700 $^{\circ}$C and a constant flow of N_2 300 to 500 cm^3/min, and activated by microwave with the assistance of $ZnCl_2$ 1.6/1 g/g within 30 min.
- The Prepared activated carbon has a surface area 709.5 m^2/g and can compete the commercial types used in water treatment.
- Olive stones, source of environment contamination, can be converted to a friendly environment material of economic and technical value.

5.1.2. Conclusion regarding nitrate removal by activated carbon

It can be concluded from the research that:

- Nitrate can be removed by AC through adsorption process with a considerable efficiency.
- It has been found that nitrate adsorption increase by decreasing pH of solution.
- The removal of nitrate from aqueous solution is affected by the contact time positively. At the equilibrium (1.5 hour) 60% of the nitrate was removed.
- Percentage of nitrate removal increases by the increase of the adsorbent dosage till 2 g level, then it became constant.
- Effect of initial concentration within the range of (20 to 120 mg/l) on adsorption was investigated. percent of nitrate removal increase with increase of initial concentration till 80 mg/l, after which it decreased. However, the increase in the removal ratio of nitrate was not significant.

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- Temperature within the range of 10 to 50 ºC has minimal effect on the removal of nitrate. This indicates that AC can be used in treatment under various temperatures without affecting the adsorbent efficiency.
- It is found that the adsorption of nitrate on PAC was better represented by the Langmuir model, while on CAC represented by Freundlich model.
- Pseudo-second order model results show better agreement with experimental data compared to other model. Therefore, it is safe to infer that nitrate adsorption systems on both PAC & CAC followed pseudo-second order kinetic model.

5.2. Recommendations for further study

- It is suggested to investigate the feasibility of producing AC from other potential biomass or agricultural waste by microwave irradiation and exam it in nitrate adsorption from water.
- It is recommended to study the using of OSAC in adsorption of other types of pollutants and contaminants from aqueous solution.
- It is suggested to study the nitrate removal onto OSAC by column study and find out some design characteristics of AC such as Empty Bed Contact Time (EBCT), Carbon usage rate (CUR), Specific throughput (ST), Mass of organic material adsorbed at breakthrough and Time to breakthrough that will help in the practical use of the AC in treatment processes.
- It is suggested to study the adsorption efficiency of OSAC on nitrate removal in real water solution.
- Further study on nitrate adsorption by using other types of AC.
- Further study on the economic feasibility of using the AC from olive stones.

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Appendices

Appendix A: Acetic acid calculation

Table (A.1): Surface area of commercial AC by acetic acid method

No.	C0 (M)	Ce (M)	C0-Ce (M)	N	Ce/N	V (ml)	V buret (ml)
1	0.015	0.00438	0.01062	0.00106	4.124294	3	1.2
2	0.0375	0.01533	0.02217	0.00222	6.91475	7.5	4.2
3	0.07	0.039055	0.030945	0.00309	12.62078	14	10.7
4	0.095	0.05913	0.03587	0.00359	16.48453	19	16.2
5	0.127	0.082125	0.044875	0.00449	18.30084	25.4	22.5
6	0.16	0.113515	0.046485	0.00465	24.41971	32	31.1

Nm = 0.00555

Surface area by acetic acid = 725.624 m^2/g

Surface area by BET method = 1100 m^2/g

Correction factor = 1100/ 725.624 = 1.516

Surface area of prepared activated carbon were calculated by using acetic acid isotherms at several activation time (5,10,20,30 and 40 min) as shown in following Tables and Figures.

Table (A.2): Acetic acid isotherm of PAC at activation time 5 min

No.	C0 (M)	Ce (M)	C0-Ce (M)	N	Ce/N	v(buret) (ml)
1	0.015	0.00445	0.01055	0.001055	4.218009	1
2	0.0375	0.015575	0.021925	0.0021925	7.103763	3.5
3	0.07	0.02581	0.04419	0.004419	5.840688	5.8
4	0.095	0.05874	0.03626	0.003626	16.19967	13.2
5	0.127	0.09434	0.03266	0.003266	28.88549	21.2
6	0.16	0.131275	0.028725	0.0028725	45.70061	29.5

Nm= 0.00246

Surface area (acetic acid) = 321.5 m^2/g

Surface area (BET) = 487 m^2/g
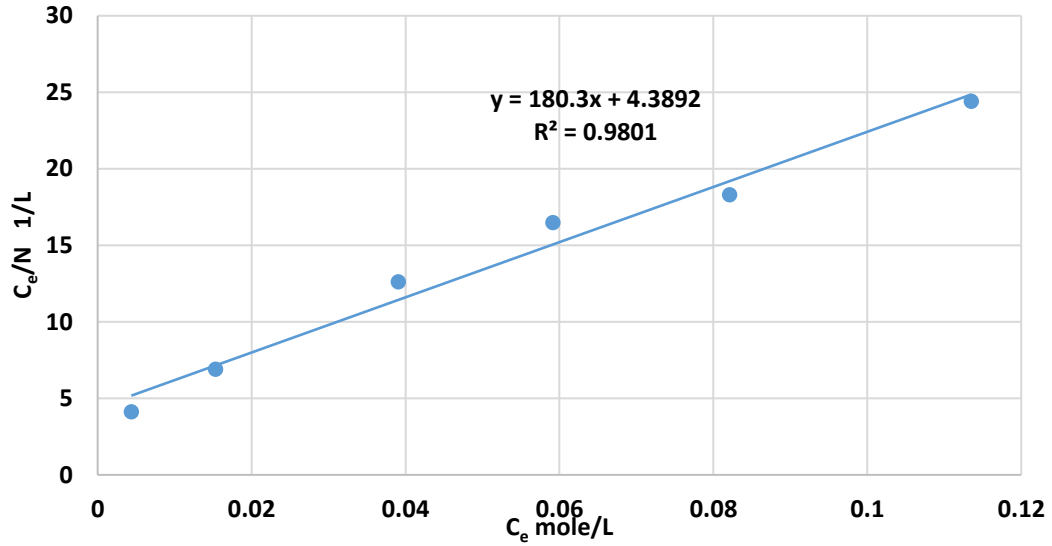
Figure (A.1): Acetic acid isotherm of PAC at activation time 5 min

Table (A.3): Acetic acid isotherm of PAC at activation time 10 min

No.	C0 (M)	Ce (M)	C0-Ce (M)	N	Ce/N	v(buret) (ml)
1	0.015	0.0089	0.0061	0.00061	14.59016	2
2	0.0375	0.023585	0.013915	0.0013915	16.94934	5.3
3	0.07	0.046725	0.023275	0.0023275	20.07519	10.5
4	0.095	0.07921	0.01579	0.001579	50.16466	17.8
5	0.127	0.10413	0.02287	0.002287	45.53126	23.4
6	0.16	0.13795	0.02205	0.002205	62.56236	31

Nm = 0.00255

Surface area (acetic acid) = 333.2 m^2/g

Surface area (BET) = 505 m^2/g

Figure (A.2): Acetic acid isotherm of PAC at activation time 10 min

Table (A.4): Acetic acid isotherm of PAC at activation time 20 min

No.	C0 (M)	Ce (M)	C0-Ce (M)	N	Ce/N	v(buret) (ml)
1	0.015	0.009345	0.005655	0.0005655	16.5252	2.1
2	0.0375	0.02403	0.01347	0.001347	17.83964	5.4
3	0.07	0.047615	0.022385	0.0022385	21.27094	10.7
4	0.095	0.07209	0.02291	0.002291	31.46661	16.2
5	0.127	0.095675	0.031325	0.0031325	30.5427	21.5
6	0.16	0.13884	0.02116	0.002116	65.61437	31.2

Nm = 0.00284

Surface area (acetic acid) = 371.4 m^2/g

Surface area (BET) = 563 m^2/g
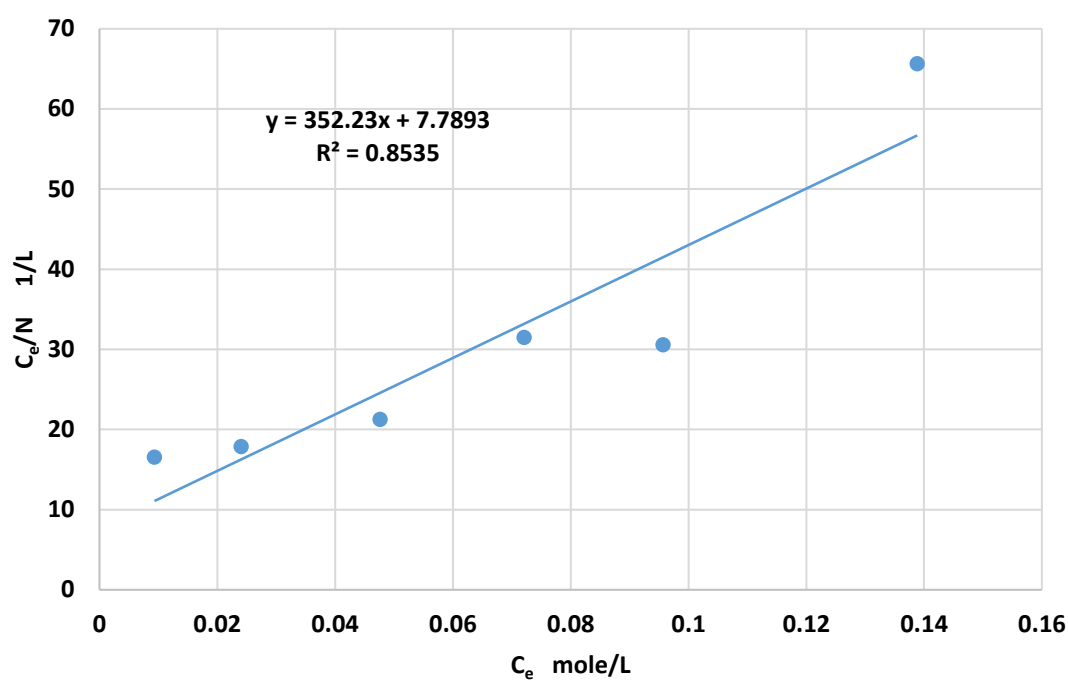
Figure (A.3): Acetic acid isotherm of PAC at activation time 20 min

Table (A.5): Acetic acid isotherm of PAC at activation time 30 min

No.	C0 (M)	Ce (M)	C0-Ce (M)	N	Ce/N	v(buret) (ml)
1	0.015	0.0109025	0.0040975	0.00040975	26.60769	2.45
2	0.0375	0.02492	0.01258	0.001258	19.80922	5.6
3	0.07	0.055625	0.014375	0.0014375	38.69565	12.5
4	0.095	0.07476	0.02024	0.002024	36.93676	16.8
5	0.127	0.10591	0.02109	0.002109	50.21811	23.8
6	0.16	0.13617	0.02383	0.002383	57.14226	30.6

Nm = 0.00358

Surface area (acetic acid) = 468.1 m^2/g

Surface area (BET) = 709 m^2/g
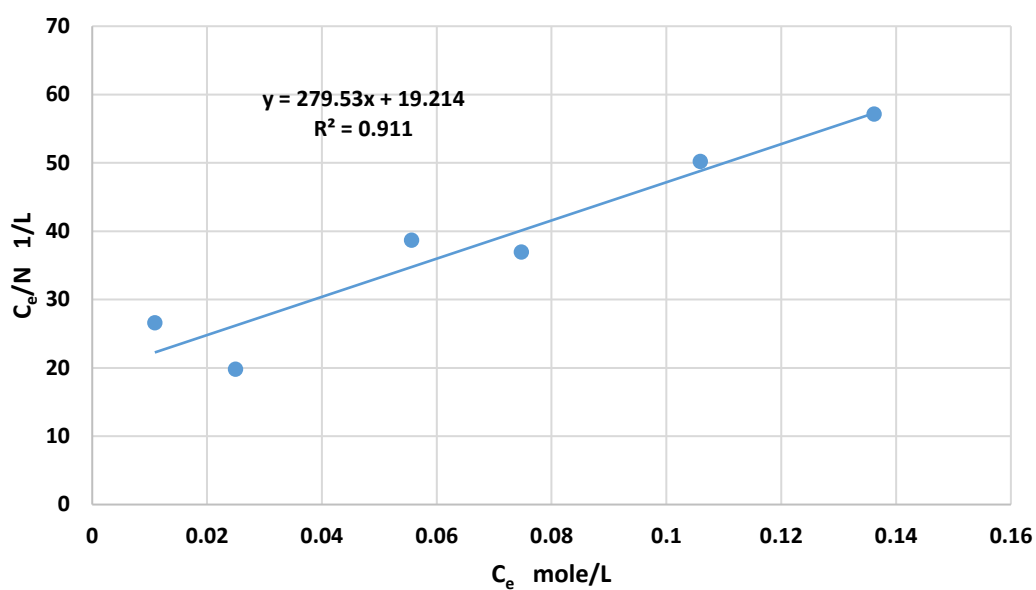
Figure (A.4): Acetic acid isotherm of PAC at activation time 30 min

Table (A.6): Acetic acid isotherm of PAC at activation time 40 min

No.	C0 (M)	Ce (M)	C0-Ce (M)	N	Ce/N	v(buret)
1	0.015	0.010235	0.004765	0.0004765	21.47954	2.3
2	0.0375	0.02403	0.01347	0.001347	17.83964	5.4
3	0.07	0.04717	0.02283	0.002283	20.66141	10.6
4	0.095	0.07743	0.01757	0.001757	44.06944	17.4
5	0.127	0.102795	0.024205	0.0024205	42.4685	23.1
6	0.16	0.135725	0.024275	0.0024275	55.91143	30.5

Nm = 0.00323

Surface area (acetic acid) = 422.6 m^2/g

Surface area (BET) = 641 m^2/g

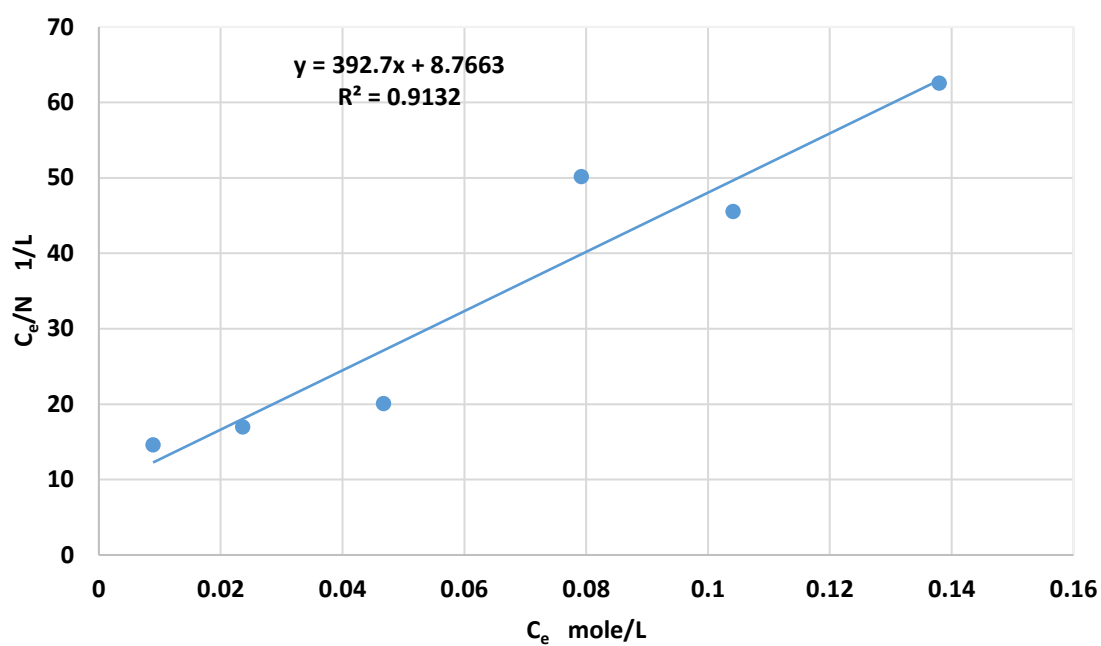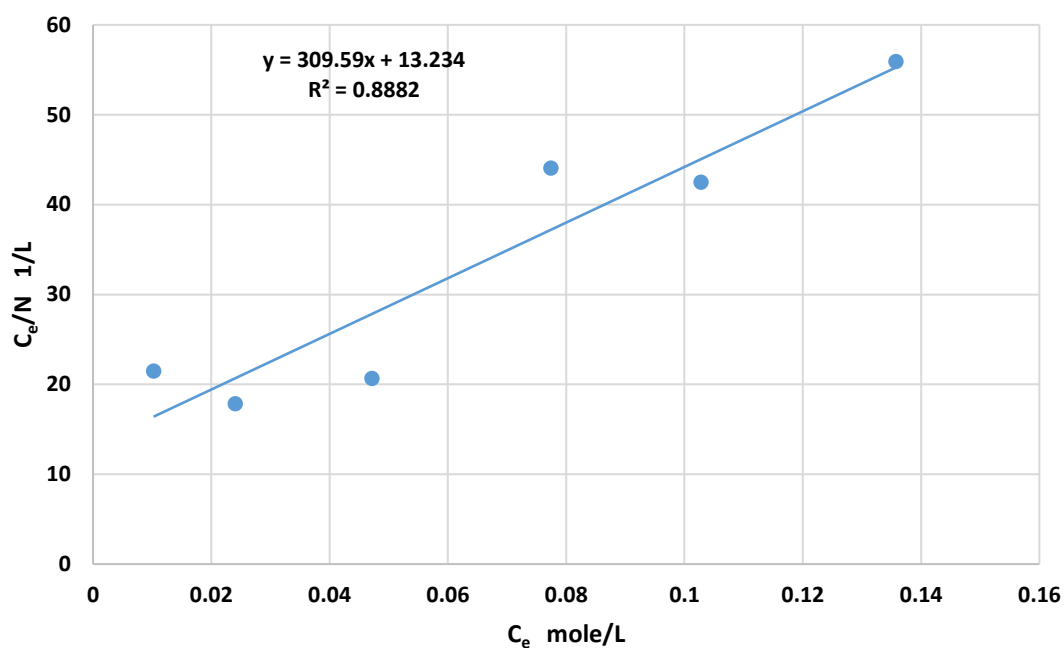**Figure (A.5):** Acetic acid isotherm of PAC at activation time 40 min

As a result for the above, the surface area of PAC at different activation time calculated are summarized in the following Table (A.7).

Table (A.7): Surface area of prepared activated carbon at several activation time

Time of activation (min)	Surface area - acetic acid (m²/g)	Surface area - BET N_2 (m²/g)
5	321.5	487.3
10	333.2	505.1
20	371.4	563.1
30	468.0	709.5
40	422.6	640.6

Appendix B: Nitrate removal

A. Standard curve of nitrate stock solution

The solution was prepared by dissolving 1.64 grams of K NO$_3$ in 1000 ml of distilled water in a volumetric flask. The standard curve of the nitrate solution was then obtained by taking a set of concentrations (0- 2.5- 5- 8- 10- 12- 15 M). Then, the values of amount of light intensity measured by UV-Spectrophotometer device are taken and then draw a standard curve as show in the Figure (B.1). Working solution was prepared at a concentration of 100 ppm instead of the original stock solution by dilution for use in subsequent tests.

y = 0.0493x + 0.0124
R² = 0.9992
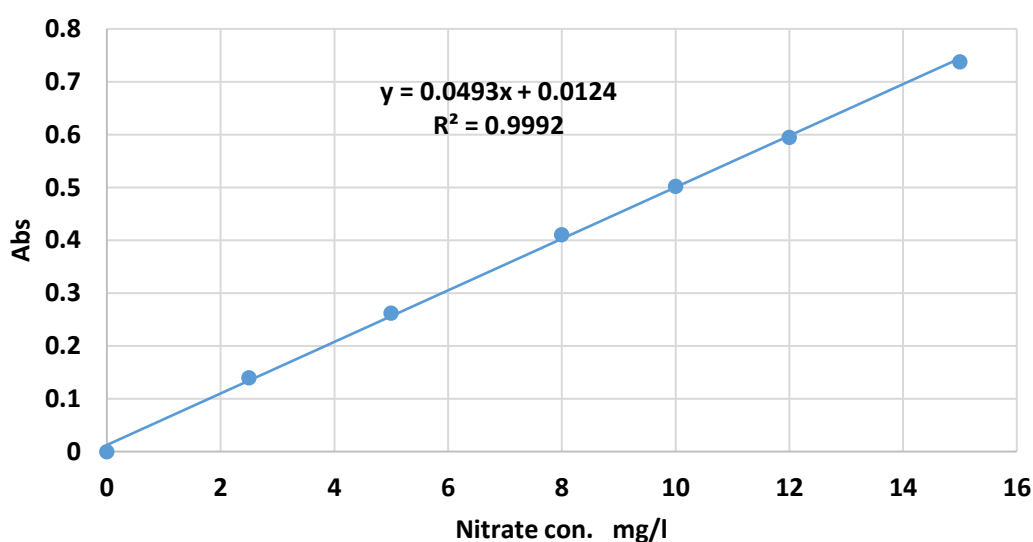
Figure (B.1): Standard curve for nitrate analysis by UV-VIS spectrometric method

B. Factors affecting adsorption

Table (B.1): Effect of solution pH on nitrate ion removal by OSAC and CAC

#	PH	CAC					OSAC				
		Abs	conc (dill)	conc (Original)	Ads.	% removal	Abs	conc (dill)	conc (Original)	Ads.	% removal
1	2	0.17	3.20	31.97	32.23	50.21	0.18	3.40	34.00	30.20	47.05
2	4	0.17	3.20	31.97	32.23	50.21	0.176	3.32	33.18	31.02	48.31

#		Abs	conc (dill)	conc (Original)	Ads.	% removal	Abs	conc (dill)	conc (Original)	Ads.	% removal
3	6	0.18	3.40	34.00	30.20	47.05	0.185	3.50	35.01	29.19	45.47
4	8	0.19	3.60	36.02	28.18	43.89	0.193	3.66	36.63	27.57	42.94
5	10	0.22	4.21	42.11	22.09	34.41	0.214	4.09	40.89	23.31	36.30

Table (B.2): Effect of contact time on nitrate ion removal by OSAC and CAC

#	T (min)	CAC					OSAC				
		Abs	conc (dill)	conc (Original)	Ads.	% removal	Abs	conc (dill)	conc (Original)	Ads.	% removal
	0.0	0.329	6.42	64.20	0.00	0.00	0.329	6.42	64.20	0.00	0.00
1	0.5	0.23	4.41	44.14	20.06	31.25	0.202	3.85	38.46	25.74	40.10
2	1.0	0.17	3.20	31.97	32.23	50.21	0.174	3.28	32.78	31.42	48.94
3	1.5	0.122	2.22	22.23	41.97	65.37	0.135	2.49	24.87	39.33	61.26
4	2.0	0.116	2.10	21.01	43.19	67.27	0.133	2.45	24.46	39.74	61.90
5	2.5	0.11	1.98	19.80	44.40	69.16	0.13	2.39	23.85	40.35	62.84
6	5.0	0.105	1.88	18.78	45.42	70.74	0.128	2.34	23.45	40.75	63.48

Table (B.3): Effect of dosage on nitrate ion removal by OSAC and CAC

#	dosage	CAC					OSAC				
		Abs	conc (dill)	conc (Original)	Ads.	% removal	Abs	conc (dill)	conc (Original)	Ads.	% removal
	0	0.329	6.42	64.20	0.00	0.00	0.329	6.42	64.20	0.00	0.00
1	0.5	0.24	4.62	46.17	18.03	28.09	0.27	5.23	52.25	11.95	18.61
2	1	0.201	3.83	38.26	25.94	40.41	0.208	3.97	39.68	24.52	38.20
3	1.5	0.161	3.01	30.14	34.06	53.05	0.156	2.91	29.13	35.07	54.63
4	2	0.121	2.20	22.03	42.17	65.69	0.127	2.32	23.25	40.95	63.79
5	3	0.117	2.12	21.22	42.98	66.95	0.127	2.32	23.25	40.95	63.79

Table (B.4): Effect of initial concentration on nitrate ion removal by OSAC and CAC

#	Co	CAC					OSAC				
		Abs	conc (dill)	conc (Original)	Ads.	% removal	Abs	conc (dill)	conc (Original)	Ads.	% removal
1	20	0.052	0.80	8.03	11.97	59.84	0.052	0.80	8.03	11.97	59.84
2	40	0.091	1.59	15.94	24.06	60.14	0.09	1.57	15.74	24.26	60.65
3	80	0.145	2.69	26.90	53.10	66.38	0.153	2.85	28.52	51.48	64.35
4	100	0.189	3.58	35.82	64.18	64.18	0.19	3.60	36.02	63.98	63.98
5	120	0.235	4.52	45.15	74.85	62.37	0.23	4.41	44.14	75.86	63.22

Table (B.5): Effect of temperature on nitrate ion removal by OSAC and CAC

#	temp	CAC					OSAC				
		Abs	conc (dill)	conc (Original)	Ads.	% removal	Abs	conc (dill)	conc (Original)	Ads.	% removal
1	10	0.142	2.63	26.29	45.71	63.49	0.148	2.75	27.51	44.49	61.80
2	20	0.137	2.53	25.27	46.73	64.90	0.145	2.69	26.90	45.10	62.64
3	30	0.139	2.57	25.68	46.32	64.33	0.142	2.63	26.29	45.71	63.49
4	40	0.14	2.59	25.88	46.12	64.05	0.144	2.67	26.69	45.31	62.93
5	50	0.138	2.55	25.48	46.52	64.62	0.148	2.75	27.51	44.49	61.80

Appendix C: Isotherm and Kinetic model

Table (C.1): Langmuir and Freundlich isotherm model for nitrate adsorption on PAC

Flask No.	M (g)	V (mL)	C (mg/l)	X (mg)	X/M	Langmuir isotherm		Freundlich isotherm	
						1/(x/m)	1/c	Log c	Log x/m
1	0.5	100	52.252	1.77	3.55	0.28	0.019	1.72	0.55
2	1	100	39.675	3.03	3.03	0.33	0.025	1.60	0.48
3	1.5	100	29.128	4.09	2.72	0.37	0.034	1.46	0.44
4	2	100	23.245	4.68	2.34	0.43	0.043	1.37	0.37
Initial	0.00	100	70.00						

Table (C.2): Kinetic models of nitrate adsorption onto PAC

Time	$C_o - C_t$	q_t	$q_e - q_t$	Log ($q_e - q_t$)	t/q	t0.5	Ct	$C_o - C_t$	Removal %
0.5	31.542	1.5771	1.9229	0.2840	0.3170	0.7071	38.458	31.542	45.06
1.0	37.221	1.8611	1.6389	0.2146	0.5373	1.0000	32.779	37.221	53.17
1.5	45.132	2.2566	1.2434	0.0946	0.6647	1.2247	24.868	45.132	64.47
2.0	45.538	2.2769	1.2231	0.0875	0.8784	1.4142	24.462	45.538	65.05
2.5	46.146	2.3073	1.1927	0.0765	1.0835	1.5811	23.854	46.146	65.92
Initial	70.0	3.5000					70.000		

Table (C.3): Langmuir and Freundlich isotherm model for nitrate adsorption on CAC

Flask No.	M (g)	V (mL)	C (mg/l)	X (mg)	X/M	Langmuir isotherm		Freundlich isotherm	
						1/(x/m)	1/c	Log c	Log x/m
1	0.5	100	46.166	2.38	4.77	0.21	0.022	1.66	0.68
2	1	100	38.256	3.17	3.17	0.32	0.026	1.58	0.50
3	1.5	100	30.142	3.99	2.66	0.38	0.033	1.48	0.42
4	2	100	22.028	4.80	2.40	0.42	0.045	1.34	0.38
Initial	0.00	100	70.00						

Table (C.4): Kinetic models of nitrate adsorption onto CAC

Time	Co - Ct	q_t	$q_e - q_t$	Log ($q_e - q_t$)	t/q	$t^{0.5}$	Ct	Co - Ct	Removal %
0.5	25.862	1.2931	2.2069	0.3438	0.3867	0.7071	44.138	25.862	36.95
1.0	38.032	1.9016	1.5984	0.2037	0.5259	1.0000	31.968	38.032	54.33
1.5	47.769	2.3884	1.1116	0.0459	0.6280	1.2247	22.231	47.769	68.24
2.0	48.986	2.4493	1.0507	0.0215	0.8166	1.4142	21.014	48.986	69.98
2.5	50.203	2.5101	0.9899	-0.0044	0.9960	1.5811	19.797	50.203	71.72
Initial	70.0	3.5000					70.000		