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MEDRC Series of R&D Reports
MEDRC Project: 12-AS-002

Removal of Detergents from Treated Wastewater by Activated Carbon produced from Olives Crushed Seeds

M. Sc. Thesis

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June 2013

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إزالة المنظفات الصناعية من مياه الصرف الصحي المعالجة بالكربون المنشط المصنع من نوى الزيتون المطحون

Removal of Detergents from Treated Wastewater by Activated Carbon produced from Olives Crushed Seeds

by

Farid Ashour

Supervised by:

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A thesis submitted in partial fulfillment of the requirements for
the degree of Master of Science in Civil Engineering

Water Resource Engineering

1434هـ - 2013م

DEDICATION

I dedicate this research 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 parents, my wife, my children, brothers, sisters, and all my friends who supported me.

ACKNOWLEDGEMENT

First, thanks to Allah, the compassionate the merciful, for giving me patience and strength to accomplish this research.

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.

My deepest gratitude to Dr. Fahid Rabah, for his supervision, encouragement and guidance of this study, and I am grateful to all doctors in the civil and environment departments of the Islamic University for their support and assistance.

I would like to thank all my colleagues in CMWU for their help and great environment that helped me in completing this research especially all of my colleagues at CMWU laboratory. Also I would like to thank Dr. Ahmad Al Mughary and his staff at Birzeit University laboratory for their remarkable support in running the experiments.

I wish also to express my love to my family for its understanding, patience and encouragement.

ملخص الدراسة

تعتبر المنظفات الصناعية من أفضل ما توصل له العلم للحفاظ علي نظافة الانسان و في نفس الوقت تعتبر طريقة التخلص منها عن طريق الصرف الصحي من أخطر مسببات التلوث للمياه السطحية و الجوفية. لذلك يبذل الباحثون جهدا عاليا لمحاولة التخلص او التخفيف من أثر هذا الملوث علي البيئة. يهدف هذا البحث الى المساهمة في ازالة المنظفات الصناعية من مياه الصرف الصحي باستخدام طريقة اقتصادية وعملية بواسطة الكربون المنشط قليل التكلفة بالاعتماد على مادة أولية متوفرة ورخيصة وهى نوى الزيتون المطحون (مخلفات عصر الزيتون). ولتحقيق هذا الهدف تم القيام بالعديد من التجارب المخبرية على إمتزاز المنظفات الصناعية بوساطة الكربون المنشّط . في بحثنا هذا تمت عملية تفحيم نوى الزيتون في درجة حرارة 500 الي 550 درجة مئويه بوجود غاز النيتروجين الخام بمعدل سريان 300 الي 500 سم^3/دقيقه و من ثم تنشيطه بواسطة الحرارة الناتجة عن الميكوويف مع اضافة هيدروكسيد البوتاسيوم للكربون بنسبة 1:2 حتى الحصول على أفضل مساحة سطحية للكربون المنشط و البالغة 540 متر مربع لكل جرام .

في عينات مائية تحاكي مياة الصرف الصحي و بوجود المنظف الصناعي LAS و تحت تأثير عوامل مختلفة مثل زمن التعريض و كمية الكربون المستخدم و درجة الحموضة وتركيز الملوثات تم التعرف علي مدى كفاءة ازالة المنظفات الصناعية بواسطة الكربون المنشط و أظهرت النتائج أنه بزيادة زمن التعريض تزداد نسبة الإزالة و تكون في الساعات الاولى من زمن التعريض أعلى. في حين أظهرت الدراسة أن معدل الإزالة للمنظف الصناعي لكل واحد غرام من الكربون المنشط يقل بزيادة كمية الكربون. كما أظهرت الدراسة أنه في معدلات درجة حموضة مياه الصرف الصحي لا يتغير معدل الإزالة بدرجة ملحوظة في حين مع إزدياد التركيز الاولِي للملوث فإن معدل الإزالة في حالة التشبع تثبت حتي تركيز 25 ملغرام/لتر و من ثم تنخفض بدرجة حادة. كما تم تفسير عملية الإمتزاز التي تم الحصول عليها عند الإتزان بإستخدام معادلة لانجمير وفرندليخ. حيث كان نموذج فرندليخ أنسب لتفسير إمتزاز LAS في التراكيز أقل من 25 ملغرام/لتر عند 25 درجة مئوية و pH 6.67 . من ناحية أخرى كان نموذج لانجمير هو الأنسب لتفسير إمتزاز LAS عند التراكيز الأعلى من 50 الي 200 ملغرام/لتر عند نفس درجة الحرارة و pH .

عند استخدام عينات صرف صحي حقيقية من مخرجات محطات المعالجة في قطاع غزة و دراسة إمكانية ازالة ما تحتويه من منظفات صناعية أبدى الكربون المنشط مقدره عاليه علي ازالة المنظفات الصناعيه و بنسبه تصل الي 42% في عشرين ساعة و في نفس الوقت إزالة COD و TKN بنسب تتراوح بين 11% و 20% .

يتضح من البحث بأن الكربون المنشط المنتج من نوى الزيتون يمكن استخدامه بكفاءة لإزالة المنظفات الصناعية في مياة الصرف الصحي بواسطة خاصية الإمتزاز و يمكن اعتباره منافسا لأنواع تجارية عديدة لما له من مميزات توازي تلك الأنواع وهذاسيكون له بالغ الأثر في إعادة استخدام المياه المعالجة في الزراعة أو حقن الخزان الجوفي.

ABSTRACT

The objective of this study is to study the possibility of removing the residual detergent from the treated wastewater by using the available materials (Olives Crushed Seeds) that resulted from Olive's mills, which contribute in contaminating the environment.

The effluent of treatment plants once treated from pollutants and detergents, it can be directed to either infiltration basins to recharge the aquifer or natural water wadis to revival the natural reserves along these wadis. The infiltrated water will be recovered and reused for irrigation.

To achieve this objective, through this research the olives crushed seeds has been carbonized at 500 - 550 ^{o}C at inert environment by flowing Nitrogen (300-500 cm^3/min) in the rector for 1hour and been activated by microwave with assistance of KOH 1:2 w/w, the resulted AC has a surface area 540 m^2/g and ash content of 1.08%.

Produced activated carbon has been used in removing detergents from synthetic and real wastewater by adsorption process under different conditions such as adsorption time, initial concentration, pH and adsorbent quantity. It has been found that the removal of LAS from synthetic solution is affected by the contact time positively as in the first 20 hours a 35% of the 10 mg/l concentrated is removed and at the equilibrium (5 days) 98% of the LAS was removed. pH within the range of 5 to 9, has no effect on the percentage removal, Initial concentration within the range of (5 to 25 mg/l) has minimal effect on the removal at equilibrium stage, while at the range greater that 25 to 200 mg/l a serious effect is clear and removal dropped from 98% to 65%. As the adsorbent quantity increases, the percentage of removal increases, however, the amount adsorbed by unit mass decreases.

Freundlich and Langmuir Isotherms, are describing the relationship between the amount of LAS adsorbed and its equilibrium concentration. Freundlich isotherm describe the relation at the range of 5 to 25 mg/l concentration while Langmuir isotherm describe the relation at the range of 50 to 200 mg/l. Results from the isotherms prove that LAS is a favorable for removal by activated carbon from aqueous solutions.

The research proof that detergent can be removed from real wastewater in addition to other substances available at wastewater such as COD and TKN.

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LIST OF ABBREVIATIONS

Abbreviation	Name
°C	Celsius
AC	Activated Carbon
BET	Brunauer, Emmett and Teller theory
BOD	Biochemical Oxygen Demand
BW	World Bank
cm^3/min	Cubic Centimeter per minute
CMWU	Coastal Municipalities Water Utility
COD	Chemical Oxygen Demand
FAO	Food and Agricultural Organization
g	grams
GAC	Granular Activated Carbon
GWWTP	Gaza Waste Water Treatment Plant
IUPAC	International Union of Pure and applied Chemistry
K	Kelvin
KOH	Potassium hydroxide
LAS	Linear Alkyl benzene Sulphonates
m3	Cubic meter
MBAS	Methylene Blue Active Substance
MCM	Million Cubic Meter
mg/L	Milligram per Liter
ml	Milliliter
mm	Millimeter
NaOH	Sodium Hydroxide
PAC	Powder Activated Carbon
pH	Hydrogen Power
PWA	Palestinian Water Authority
RWWTP	Rafah Waste Water Treatment Plant
SEM	Scanning Electronic Microscope
TKN	Total Kjeldahl Nitrogen
TSS	Total Suspended Solids

UNRWA	United Nations for Refugees Working Agency
W/W	weight to weight ratio
WHO	World Health Organization
WHO	World Health Organization

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CHAPTER 1: INTRODUCTION

1.1 Background

Middle East and North Africa region is the most water scarce region of the world, where, aquifer are over-pumped, water quality is deteriorating and water supply and irrigation services are often share with consequences for human health, agricultural productivity and negative impact on the environment. It is still known in the Middle East that water resources is one of the main reasons for the current dispute and conflicts between the trans-boundary countries and the conflicts will get worse when knowing that the resources are in depletion and most of the region's countries cannot meet current water demand. Indeed, many face full-blown crises. The per capita water availability will fall by half by 2050, with serious consequences for the region's already stressed aquifers and natural hydrological systems. (World-Bank, 2007)

Palestine as one of the Middle East countries, which have in addition to the limited and scarce, water resources, has either limited or denied accessibility to these resources, and it is controlled by the regulations of the Israeli government.

Palestinians have access to one fifth of the resources of the Mountain Aquifer and abstract about 20% of the "estimated potential" of the aquifers that underlie both the West Bank while in Gaza strip only 5-10% of the aquifer is now yielding drinking water quality (World-Bank, 2009).

Ongoing deterioration of the water supply of Gaza poses a major challenge for water planners and the sustainable management of the coastal aquifer. The aquifer is presently being over exploited, with total pumping exceeding total recharge. In addition, anthropogenic sources of pollution threaten the water supplies in major urban centers.

In the Gaza strip, the recorded water abstraction from the aquifer for domestic and agricultural needs is 164 MCM/ year, where the overall returned is only 122 MCM/year, this means that there is a deficit of about 42 MCM/year (Hamdan, et al., 2011).

Therefore, the reuse of treated wastewater has been taking an increasing interest in Palestine and has a major priority, as confirmed by the Palestinian Water Policy adopted by the PWA (Palestinian Water Authority) and the Ministry of Agriculture.

As recorded by CMWU, Currently 100 to 110 million liters per day of wastewater are collected through the existing cesspits and the network in Gaza Strip, about 80 to 90 million liters discharged to the sea as raw or partially treated wastewater from the overflow of the pump stations and treatment plants. Only 15 million liters with bad quality are infiltrated in a designed infiltration basins east side of Gaza strip. (Ashour, 2011)

Within the coming few years a three regional wastewater treatment plants will be constructed with a capacity of 180 thousand cubic meter a day, and will be able to remove pollutants such as organic load and suspended solids and reduce Nitrogen, concentrations and partially will remove organic detergents.

The effluent of these treatment plants will be directed to either infiltration basins to recharge the aquifer or natural water wadis to revival the natural reserves along these wadis. The infiltrated water will be recovered and reused for irrigation.

Although the wastewater will be treated in these treatment plants and the soil will act as a filter to remove the remaining suspended solids and microorganisms from it, some pollutants will remain, such as detergents.

Detergents that exist in the produced wastewater in Gaza strip has not been recorded periodically in the treatment plants laboratories as this test cost a lot and has side health effect, only some samples has been taken from the effluent of Gaza wastewater treatment plant and close wells to infiltration basins and detergent has detected (25 mg/l). Scientifically it is known that some degradable detergents can be removed through the secondary treatment but non-biodegradable detergents are not removed through the wastewater treatment process and remain in the effluent as a residual and in many references, it is named as (inorganic surfactants).

Recently at this study samples from GWWTP and RWWTP has been taken and detergent has been measured at the influent and the effluent and the results were (10 mg/l and 5 mg/l) respectively

The aim of this study is to investigate the potentiality of removing of the inorganic detergents from treated wastewater by using the adsorption characteristic of the activated carbon produced from olives crushed seeds.

1.2 Problem Statement

Removal of detergents is of great importance to satisfy the increasing demands for the treated wastewater for infiltration and irrigations. These detergent compounds do not decompose or degrade in secondary wastewater treatment units existing in Gaza strip, or will be constructed later, these detergents will remain in the effluent creating many problems such as affecting plants' growth, disrupting the natural percolation of the soil (the more detergents in the soil, the less water will reach plants' roots), in addition soapy water is likely to wash necessary nutrients out of the soil and away from plants' roots damaging them through nutrient imbalance and deficiency (Kroontje, et al., 1973).

Through this thesis, an experimental study will be run to investigate the potential of removing the residual inorganic detergents from treated wastewater, by activated carbon produced from olives crushed seeds, which will help in completing the treatment of this effluent to be suitable for reuse in irrigation without harming the plants or concentrated in the soil layers.

1.3 Research Aim

To study the potential of removing of the residuals detergents from the wastewater effluents using activated carbon produced from olives crushed seeds.

1.4 Research Objectives

The overall objectives of this study are:

- Studying the possibility of producing AC from Olives Crushed Seeds with comparable adsorption Capacity to other available AC.
- Studying the potential of residual detergents removal from TWW by the produced AC.
- Study the effects of detention time, AC mass dosage, initial concentration and pH on AC detergent adsorption capacity using synthetic WW.
- Producing the Adsorption Isotherms of the Olives Crushed Seeds AC for LAS detergent removal.

- Studying the characteristics of detergent removal from real WW under varied initial Concentration
- Proposing recommendations to decision makers regarding the possible use of AC in Gaza WWTPs

1.5 Research Importance

The importance of this study has two dimensions; improving treated wastewater quality, to match the required standards for reusing it in irrigation and recharging aquifer which will be reflected on the aquifer positively by minimizing abstraction for irrigation and give the aquifer a time to be recovered.

The second importance is to eliminate a pollutant from the environment and convert it to an economical product and environment friend materials through converting the crushed olives seeds to activated carbon.

1.6 Research Methodology

Working in the thesis will be divided into the following phases:

1.6.1 Data collection and desk study:

Data will be collected from local authorities like ministry of economic and local market to find out the amount of detergents and surfactants entering the local market in Gaza strip find out the types of detergents used in Gaza and the mostly used one.

1.6.2 Producing activated carbon from olives crushed seeds:

Samples of Olive crushed seeds (Olives Solid Waste) will be collected from local Olive mills, and convert it to Activated Carbon (AC) by burning it at high temperature in an inert atmosphere (***Carbonization***).

The char will be ***Activated*** using the heat produced from microwave with assistance of chemical compound such as KOH at inert situation (Nitrogen Gas). Experiments will be implemented to find out some characteristics of the produced activated carbon such as the specific area, ash content, specific weight and compare the results with commercial and known activated carbon used in the local market.

1.6.3 Potential of removing detergent by produced activated carbon.

Experimental tests will be done to find out the potential of removing detergents by produced activated carbon from wastewater samples. The tests will be using a synthetically samples with different concentrations of the detergents, time of adsorption, quantity of adsorbent, and pH. Activated carbon will be tested in removing detergent from real samples collected from wastewater.

1.6.4 Detergent concentration in wastewater and removal from real wastewater

Experimental tests will be done to measure the concentration of detergents in the wastewater; composite samples will be collected from the inlets and outlets of the treatment plants at different locations within Gaza strip.

A study for the efficiency of the existing wastewater treatment plants in removing detergent through the secondary units.

1.6.5 Recommendations and proposals

Based on the results of the experiments recommendations will be raised to be included in wastewater treatment for removal of detergent and prepare a procedure for using the results of the thesis in cleaning wastewater from these types of detergents at the farm scale.

CHAPTER 2: LITERATURE REVIEW

2.1 Wastewater production and reuse

In a global level, and in the 20th century water use has been grown more than twice the rate of population increase and reach to level where reliable water services can no longer be delivered in many regions (FAO, 2012)

Despite water scarcity and high agricultural water consumption in the Middle East and North Africa region, substantial amounts of treated wastewater are discharged into seas without proper utilization (Abu Madi, et al., 2003). In Gaza Strip, there are large quantities of wastewater estimated at 40 MCM/year are produced by the municipal sewerage systems (Hamdan, et al., 2011). 32 MCM/year are disposed to the sea or flooded without good treatment or control to the surrounding areas and underground aquifer (CMWU, 2008), while in the West Bank a 31 MCM/year of wastewater is collected, and 75% is discharged directly into the environment without any treatment (McNeill, et al., 2008).

Since the establishment of the Palestinian Authority in the mid–nineties, many central wastewater treatment plants have been planned and designed for construction. According to the plans, about 20 wastewater treatment plants should be constructed in the coming 20 years in Gaza and West Bank. The treated effluents of these plants are being considered as a strategic non-conventional water resource and should be used in agriculture and industry or where ever applicable (Kittani, 2008).

The agricultural demand in Gaza Strip is almost constant since the agricultural areas are limited or even decreasing. However, the domestic demand increases due to the rapid growth of the population. This increases the amount of wastewater produced and the treated effluent becomes a signifcant resource of water that could improve the water balance in the region (Hamdan, et al., 2011).

The Palestinian Water Authority (PWA) as the key regulator of the Palestinian water resources has developed a set of strategies for reuse of treated wastewater. These strategies are:

Reuse of treated wastewater must be considered in all treatment schemes. Cooperation must be established with different relevant bodies; for every reuse project, beneficiaries must be involved in all project phases. Flexible reuse plans should be developed to be able to utilize treated wastewater in winter seasons and when the effluent quality drops below the demands. Establish planning tools (regulations, standards, guidelines, etc.) for reuse and recharge. (Almasri, et al., 2008).

It is recognized that in order for wastewater reuse to become an established resource, a firm national water reuse policy is needed. In terms of water quality standards. Most of countries in the Mediterranean and North Africa region have not adopted water reuse standards, only a few countries have been re-assessed to meet WHO and FAO guidelines (world-Bank, 2004).

In Palestine, since 2000 a draft guideline has been prepared reflecting the expected fields (Direct Irrigation, infiltration, dumping to the sea and other) of using the treated wastewater with the required characteristics (BOD, TSS, TKN, Detergent etc). Up-to-date a final and revised guideline has not been published.

The main concerns in water reuse are proper treatment of the effluent so that it meets the quality requirements of the intended reuse, and public acceptance of potable reuse. Wastewater is a valuable resource, however without a properly developed framework policy, safe and efficient management of this resource cannot be achieved (Fatta, et al., 2005). Without proper treatment, the residual contaminants will remain an obstacle for reusing this resource, and the concern for human health and the environment are the most important constraints in the reuse of wastewater (Fatta, et al., 2005).

The most important types of the residual contaminants can be summarized by: organic matter, Nitrate, Pathogens, Detergents, Phosphorus.

2.2 Soap, Detergents and surfactants

Since the end of the last century a large amount of products, such as medicines, disinfectants, laundry detergents, surfactants, pesticides, dyes, paints, preservatives, food additives, and personal care products, have been released by chemical and pharmaceutical industries threatening the environment and human health (Grassi, et al., 2012). The conventional wastewater treatment plants are not always effective for the removal of these huge classes of pollutants and so further water and wastewater treatments are necessary (Grassi, et al., 2012).

In chemistry, **soap** is a salt of a fatty acid. Soaps are mainly used for washing, bathing, and cleaning and textile spinning. Soaps for cleansing are obtained by treating vegetable or animal oils and fats with a strongly alkaline solution. Fats and oils are composed of triglycerides; three molecules of fatty acids are attached to a single molecule of glycerol. The alkaline solution, often called lye, brings about a chemical reaction known as saponification. In saponification, the fats are first hydrolyzed into free fatty acids, which then combine with the alkali to form crude soap. Glycerol (glycerin) is liberated and is either left in or washed out and recovered as a useful byproduct, depending on the process employed (Wikipedia-Soap, 2012).

When used for cleaning, soap serves as a surfactant in conjunction with water. The cleaning action of this mixture is attributed to the action of micelles, tiny spheres coated on the outside with polar hydrophilic (water-loving) groups, encasing a lipophilic (fat-loving) pocket that can surround the grease particles, causing them to disperse in water. The lipophilic portion is made up of the long hydrocarbon chain from the fatty acid. Whereas oil and water normally do not mix, the addition of soap allows oils to disperse in water and be rinsed away (Wikipedia-Soap, 2012).

A **detergent** is a surfactant or a mixture of surfactants with cleaning properties in dilute solutions. These substances are usually alkylbenzenesulfonates, a family of compounds that are similar to soap but are more soluble in hard water, because the polar sulfonate (of detergents) is less likely than the polar carboxyl (of soap) to bind to calcium and other ions found in hard water. In most household contexts, the term detergent by itself refers specifically to laundry detergent or dish detergent, as opposed to hand soap or other types of cleaning agents. Detergents are commonly available as powders or concentrated solutions. Detergents, like soaps, work because they are amphiphilic: partly hydrophilic (polar) and partly hydrophobic (non-polar). Their dual nature facilitates the mixture of hydrophobic compounds (like oil and grease) with water. Because air is not hydrophilic, detergents are also foaming agents to varying degrees. (Wikipedia-Detergent, 2012).

Laundary Detergen; is one of the largest applications of detergents is for cleaning clothing. The formulations are complex, reflecting the diverse demands of the application and the highly competitive consumer market. In general, laundry detergents contain water softeners, surfactants, bleach, enzymes, brighteners, fragrances, and many other agents. The formulation is strongly affected by the temperature of the cleaning water and varies from country to country. (Wikipedia-Detergent, 2012).

Surfactants are compounds that lower the surface tension of a liquid, the interfacial tension between two liquids, or that between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. (Wikipedia-surfactant, 2012)

Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their *tails*) and hydrophilic groups (their *heads*). Therefore, a surfactant contains both a water insoluble (or oil soluble) component and a water soluble component. Surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. The insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water soluble head group remains in the water phase. This alignment of surfactants at the surface modifies the surface properties of water at the water/air or water/oil interface. (Wikipedia-surfactant, 2012)

Synthetic surfactants consist mainly of three types: anionic, nonionic and cationic. Linear Alkyl benzene Sulphonates (LAS), alkylethoxy sulphates (AES), alkyl sulphates (AS), alkyl ethoxylates (AE), and quaternary ammonium compounds (QAC) are the commonly used commercial surfactants. LAS are the most popularly used synthetic anionic surfactants. It has been extensively used for over 30 years with an estimated global consumption of 2.8 million tons in 1998 (Verge et al., 2000), while the world production of synthetic surfactants amounts to 7.2 million tons annually in the same year (Ying, 2006) and raised to 12.5 Million tons in year 2006 (Behler, 2008). Commercially available products are very complex mixtures containing homologues with alkyl chains ranging from 10 to 13 carbon units (C10eC13 LAS) (Becagli, *et al*, 2011), following Table 2.1, is sourced from (Ying, 2006) that summarize the different types and names of the surfactants:

Table 2.1: Acronyms of the most widely used surfactants

Class	Common name	Acronym
Anionic surfactants	Linear alkyl benzene sulphonates Secondary alkane sulphonates Alcohol ether sulphates (Alkyl ethoxy sulphates) Alcohol sulphates (Alkyl sulphates)	LAS SAS AES AS
Nonionic surfactants	Alkylphenol ethoxylates Nonyl phenol ethoxylates Octyl phenol ethoxyales Alcohol ethoxyaltes	NPE (or NPEO) APE (or APEO) OPE (or OPEO) AE (or AEO)
Cationic surfactants	Quaternary ammonium-based compounds Alkyl trimethyl ammonium halides Alkyl dimethyl ammonium halides Alkyl benzyl dimethyl ammonium halides Dialkyl dimethyl ammonium halides Dihydrogenated tallow dimethyl ammonium chloride Ditallow trimethyl ammonium chloride Diethyl ester dimethyl ammonium chloride	QAC TMAC DMAC BDMAC DADMAC DHTDMAC or DTDMAC DTTMAC DEEDMAC

2.2.1 Surfactant and Detergents Impacts on Environment

An increased awareness of environmental quality has resulted in the detailed examination of options for the management of wastewater and sludge. The transport of water and chemicals through soils is governed by factors such as the type of solute, soil moisture conditions and physical and hydraulic properties of the soils. Detergents, containing anionic and non-ionic surfactants, account for the highest concentrations of organic chemicals found in wastewater and sludge. (Abu-Zreig, et al., 2003)

Surfactants are widely used in household and industrial products. After use, surfactants as well as their products are mainly discharged into sewage treatment plants and then dispersed into the environment through effluent discharge into surface waters and sludge disposal on lands, (Ying, 2006) the main hazard of detergent pollution lays in their effect on water ecosystems as a whole. In the first instance, surfactants may adversely affect microalgae at the lowest trophic level and impact on their function as major suppliers of oxygen to water bodies. (Orkide, et al., 2009)

Detergents affect receiving aquatic environments by causing foaming, limiting oxygen production, causing eutrophication and presenting a hazard to waters used for potable supply. Surface foams may block aeration of water bodies and their decomposition may increase biochemical oxygen demand and thereby deplete dissolved oxygen levels. Moreover, detergent concentrations greater than 0.1 mg/l are toxic to some marine organisms. Sub-lethal concentrations may affect other life stages of marine organisms, notably ovum and larval stages. (Orkide, et al., 2009)

Therefore, it is very important to check the degradability of the surfactant, as degradation of surfactants through microbial activity is the primary transformation occurring in the environment. Biodegradation is an important process to treat surfactants in raw sewages in sewage treatment plants, and it also enhances the removal of these surfactants in the environment, thus reducing their impact on biota. During biodegradation, microorganisms can either utilize surfactants as substrates for energy and nutrients or co-metabolize the surfactants by microbial metabolic reactions. Many chemical and environmental factors affect biodegradation of a surfactant in the environment. The most important influencing factors are chemical structure, and physiochemical conditions of the environmental media. Different classes of surfactants have different degradation behavior in the environment. Microbes in the environment can degrade most of the surfactants, although some surfactants such as LAS may be persistent under anaerobic conditions. (Ying, 2006)

On the other hand, some types of surfactants are formulated to facilitate or improve the emulsifying, dispersing, spreading, sticking or penetrating of liquids. Surfactants were initially used to enhance the penetration and effectiveness of foliar applied herbicides, defoliants, and insecticides by decreasing surface tension of aqueous systems. Now, surfactants have broader and more intensive use in immunoassays, biosynthesis of nucleic acids, floral induction, soil wetting, fruit thinning, hormone interactions, and photoperiodicity. (Myers, 2006)

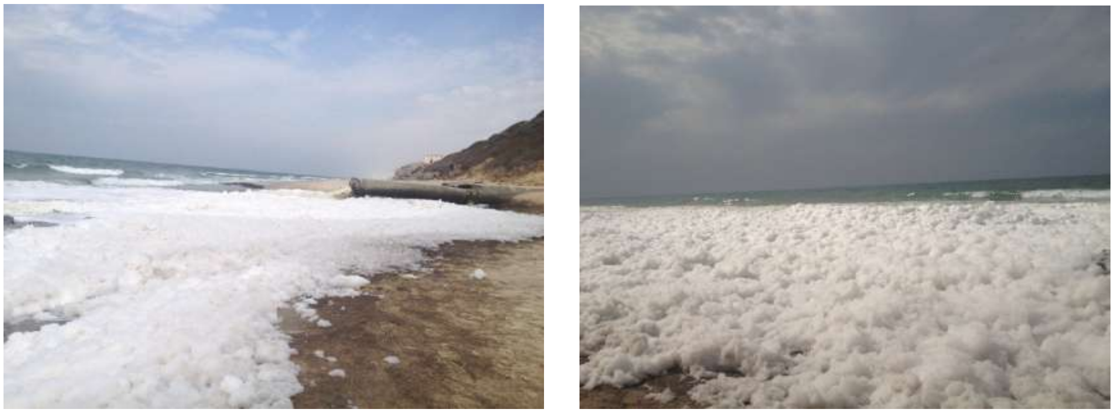
2.2.2 Cleaning and washing materials in Gaza Strip

The data collected from the ministry of the Economy shows the quantities of the washing and cleaning materials that crossing the border to Gaza strip, there is no classification recorded in the ministry and a general test proof that the mostly type used in Gaza is Linear alkyl benzene sulphonates, the following Table 2.2 shows these quantities;

Table 2.2: Cleaning and Washing materials enter Gaza Strip

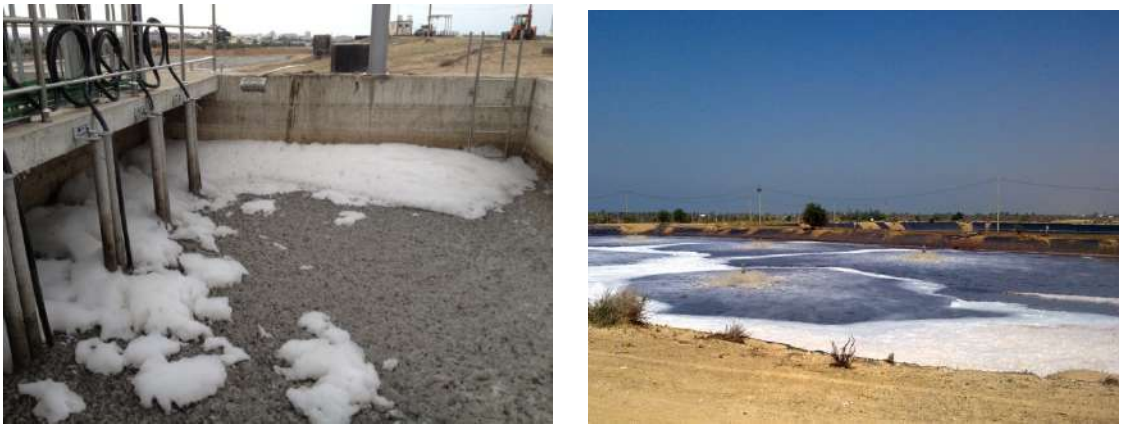
Type Month	**Year 2009**		**Year 2010**	
	Cleaning & Washing Materials	Raw materials	Cleaning & Washing Materials	Raw materials
	ton	ton	ton	ton
Jan	330	0	1,215	0
Feb	0	0	823	0
Mar	1,585	0	1,824	0
Apr	9,850	0	946	0
May	6,377	0	1,031	0
Jun	2,172	0	1,385	0
Jul	1,602	0	918	0
Aug	2,303	0	1,062	1,327
Sep	1,089	0	699	869
Oct	1,646	0	1,240	1,115
Nov	2,287	0	1,112	712
Dec	2,085	0	1,084	1,044
Total	**31,326**	**0**	**13,339**	**5,067**
	Year 2011		**Year 2012**	
Jan	1,133	486	1,044	883
Feb	930	519	1,618	489
Mar	1,190	517	1,159	370
Apr	492	394	1,033	901
May	978	775	1,483	701
Jun	1,032	453	1,119	754
Jul	644	759	1444	0
Aug	1,429	489	1473	0
Sep	706	377	1624	0
Oct	895	267	1438	0
Nov	1,453	811	1167	0
Dec	1,044	689	2242	0
Total	**11,926**	**6,536**	**14,602**	**4,098**

Poorly degradable surfactants remains as a residual in the effluent of the wastewater treatment plant, this can be seen in Gaza strip at all the locations of the outfalls and at aerated lagoons, pump stations, following in Figure 2-1 are some locations where foam resulted from detergents and surfactants can be noticed:



Gaza sea outfall

Sea beach and detergent foam



Pump stations at Gaza

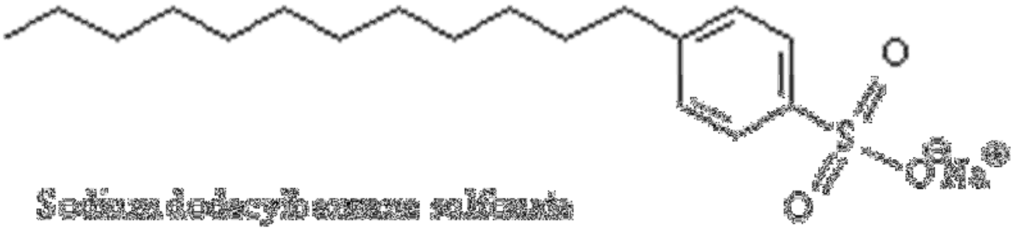
Aerated lagoons at Gaza

Figure 2-1 Detergents at wastewater facilities in Gaza

2.2.3 Linear Alkyl benzene Sulphonates (LAS)

As the mostly used type of detergent in washing worldwide is LAS, following are some characteristics about the LAS:

"LAS is an anionic surfactant i.e. the surface-active part is a negatively charged ion in water. The linear alkyl chain makes the molecule more biodegradable than alkyl benzenesulfonates with branched carbon chains. The length of the alkyl chain is not always very specified for the substances used as surfactants as it is dependant on the alkyl chain raw material." (KEMI, 2003)



"LAS is manufactured by addition of a-olefiner (the alkyl chain to be) of required length to benzene. These, in turn, are produced by uniting four, five ethene and/or propene units, by extracting normal paraffines from kerosine by molecular sieve or by cracking petroleum wax. After the alkyl benzenes have been formed they are sulfonated with sulphuric acid to alkylbenzene sulfonic acids. The acid is neutralized with e.g. sodium hydroxide for use in water-based systems or calcium hydroxide for oil based products. Neutralizing with ammonium ion, e.g. triethanolamine, generates tensides with emulsifying properties in both water and oil based systems" (Östman, 2003).

"LAS has good ability to remove and keep particles in dispersion. This is utilized in detergents for textile to remove inorganic dirt like earth. The alkyl chain of the molecule adhere to the solid surface that mostly has a faint negative charge while the likewise negatively charged sulfonic group tries to reach as far out as possible into the water phase and by this keeps the particle in dispersion. LAS are stable against oxidation making them suitable to use in mixtures containing oxidants like e.g. bleaching agents. They do not work well in hard water where water insoluble calcium soaps are precipitated" (KEMI, 2003).

2.3 Olives production

Demand for olive has increased significantly in recent years, largely in response to the increased publicity of associated health benefits for non-saturated vegetable oils. Some of the promoted beneficial attributes of olive oil include being a source of antioxidants, vitamin E, and monounsaturated fat, which helps to prevent cardiovascular disease. In addition, the satiating effect of olive oil is thought to encourage reduced calorie intake.

Figure 2-2, shows the increase of the production and the demand for the period 1990 till 2011 (source: International Olive Council November 2012) (OLIVAE, 2012)

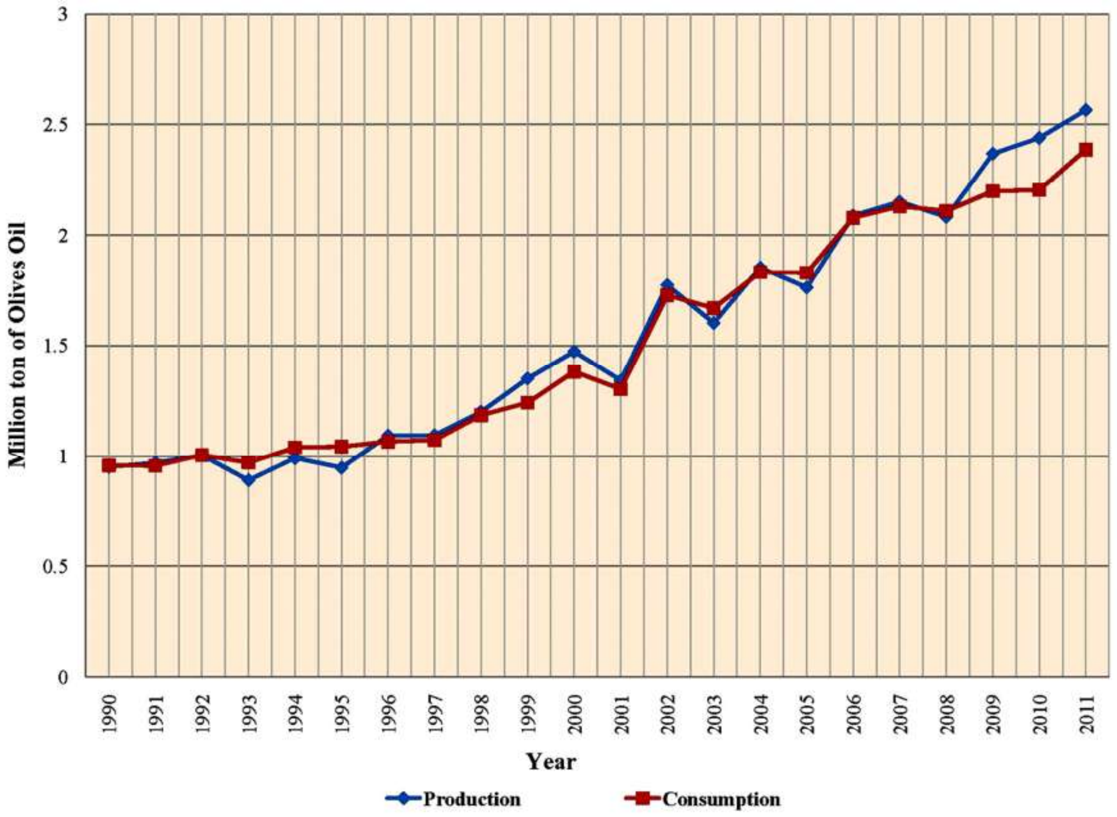


Figure 2-2 Olives oil production & consumption (OLIVAE, 2012)

Over 750 million olive trees are cultivated worldwide, 95% of which are in the Mediterranean region. Most of global production comes from Southern Europe, North Africa and the Near East. (Kostas, et al., 2006). Table 2.3 shows the average production of olive oil for the period of 2006 to 2011 (International Olive Oil Council, November 2011)

A total amount of olives oil produced at year 2011/2012 is estimated with 2,530,000 ton (OLIVAE, 2012), where the traditional pressing system generates olive oil and two kinds of by-products: waste water and pomace (olive husk). An average of 17% of the olive weight is oil, a 75% is virgin olive pomace, and the remaining percentage is water (Intini, et al., 2011). By calculating the amount of pomace production based on the above figures it give us 11,160,000 ton, where part of this solid byproduct used today to produce pomace oil; as a fertilizer in the agricultural sector and as fuel for heating. Other part is dumped to the environment as a solid waste, while most of the quantities of wastewaters which are slightly acidic and associated with high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), up to 100 and 220 g/L, respectively (Zaharaki, et al., 2009) find its way to the sewerage system and treatment plants. This high concentration of biological load affect the treatment process if not considered in the design of the plant or treated before reaching the treatment plant.

Table 2.3: Production of Olive oil (Average 2006 to 2011)

Country	Production 1000 metric ton	Percentage	Country	Production 1000 metric ton	Percentage
Albania	18	0.83%	**Syria**	136.2	6.32%
Algeria	100.4	4.66%	**Tunisia**	19.9	0.92%
Argentina	137.5	6.38%	**Turkey**	290	13.45%
Croatia	1.3	0.06%	**EU**	703.3	32.62%
Egypt	352.8	16.36%	**Saudi Arabia**	4.1	0.19%
Iran	34.2	1.59%	**Australia**	3.1	0.14%
Iraq	2	0.09%	**Brazil**	0.1	0.00%
Israel	14.8	0.69%	**Chili**	20.5	0.95%
Jordan	31.9	1.48%	**USA**	78.1	3.62%
Lebanon	15.3	0.71%	**Mexico**	9	0.42%
Libya	3	0.14%	**Palestine**	8.8	0.41%
Morocco	98.3	4.56%	**Peru**	58.4	2.71%
Montenegr	0.3	0.01%	**Other**	15	0.70%

Source: (International Olive Oil Council, November 2011)

2.3.1 Olive Mills in the Gaza Strip and West Bank

There are 299 olives mills in West Bank and the Gaza strip, in the year 2011, where 272 are operating in a good condition and about 27 are temporarily closed. 240 of these mills are fully automatic and 32 are half automatic or traditional process. Following Figure 2-3 show the distribution of the olives mills in the Gaza strip and West Bank. (PCBC, 2012)

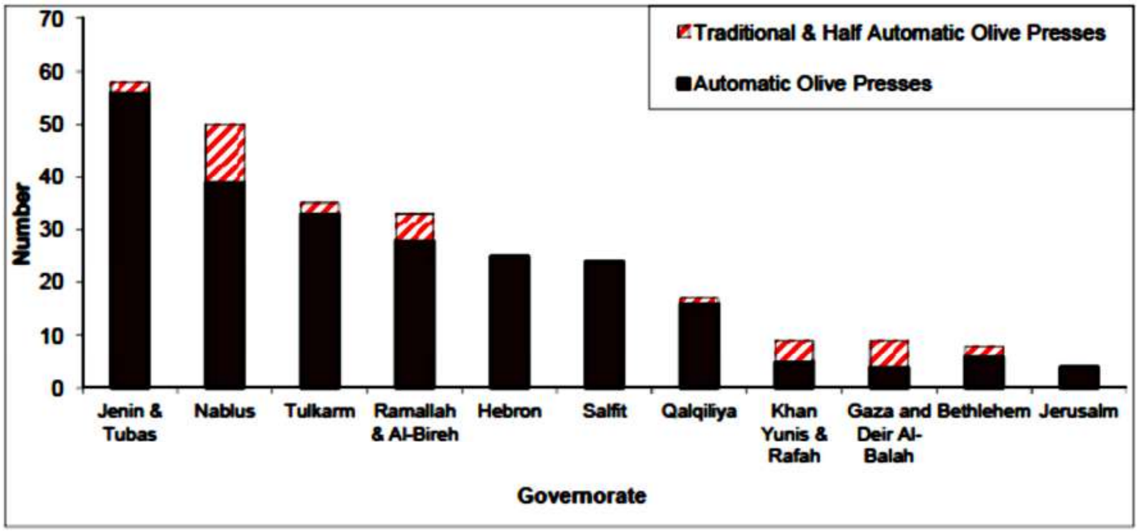


Figure 2-3 Olives Mills in the Gaza Strip and West Bank (PCBC, 2012)

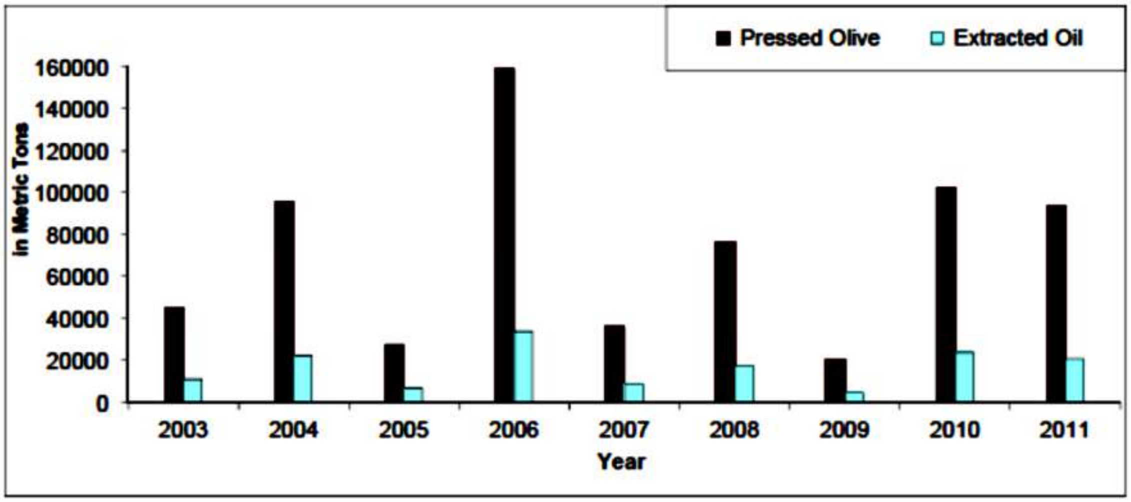


Figure 2-4 Olives Pressed and Oil production in the Gaza Strip and West Bank (PCBC, 2012).

The majority of olive presses used a tight cesspit to dispose of the liquid waste (45.2%) and Wastewater (36.4%). The majorty of the crushed olive seeds returned to the olive owners as energy source(88%) and part of it is disposed to the environment (12%) (PCBC, 2012).

2.4 Activated Carbon

Activated carbon is a material with highly porosity, its consist of hydrophobic graphene layer as well as hydrophilic surface functional groups, that make them beneficial for sorption and catalytic applications. It is used in specific industrial applications such as; oil and natural gas, food, pharmaceuticals, water treatment, hydro metallurgy, gold recovery and carbon-in-pulp process (Mansooreh, et al., 2008). Activated carbon materials are effective in removing pollutants (both gaseous and liquid). The advantage of activated carbon materials as adsorbents is that the treated effluent is of high quality, the design of the process is simple, the operation of the process developed or adopted is easy. In addition carbon materials are resistant to corrosive (acidic and basic) and toxic environments (Xiaoge, et al., 2002). In addition to purification of gases and liquids with high adsorption potential, activated carbon materials are also used as catalysts and catalyst supports.

The demand of activated carbon is increasing owing to the increased utility of the carbon materials in pollution control. As a result, cost of activated carbon is also growing depending on the application. Designing ways for the production of activated carbon through economic ways is the need of the hour. A range of low cost, easily available, carbon rich and low ash precursors and sources are being explored for the production of carbon materials. (Viswanathan, et al., 2009)

Most of the commercial activated carbons are either coal based or petroleum pitch based which are prone to exhaustion. Their global distribution is non uniform. As the applications of activated carbon are immense, the gap between demand and supply is ever widening. This may in due course result in scarcity of the material in addition to becoming expensive. This situation necessitates the need for the exploration of new sources of carbon materials with desired physico chemical properties namely, high specific surface area, micro or meso porosity or both, depending on the end application, surface functionality, thermal stability, carbon purity, adsorptive capacity and chemical composition. (Viswanathan, et al., 2009)

Lignocelluloses materials have been and will be with humankind forever and they hold a promise of renewable and inexhaustible supply of carbon materials provided suitable methods of production be developed. In addition, they are more evenly distributed throughout the globe relative to either coal or petroleum. Thus the lignocelluloses material, a re-generable natural resource, is a viable option for the generation of carbon materials rather than fossil fuels. This can be summarized with the wide variety of raw materials such as: Coconuts and seed shell of palm tree (Gueu, et al., 2006), barley straw (Husseien, et al., 2007), Neem Husk (Azadirachta Indica and Alau, et al., 2010), Cocoa pod husk (Cruz, et al., 2012 and Foo, et al., 2011) sewage sludge (Mansalvo, et al., 2011), waste tea ((Yagmur, et al., 2008), bamboo (Liu, et al., 2010), tobacco stem (Li, et al., 2007), date stone (Foo, et al., 2011), pistachio nut (Foo, et al., 2011), cotton stalks (Deng, et al., 2010), Olives stone and Olive waste cake (Bla´zquez, et al., 2004; Aljundi, et al., 2008; Baccar, et al., 2008; El-Hamouz, et al., 2006; El-Sheikh, et al., 2003; Mart´ınez, et al., 2005; Moreno-Castilla, et al., 2000; Rodrıguez, et al., 2007; Spahis, et al., 2007; Stavropoulos, et al., 2005; Ubago-Pe´rez, et al., 2006 and Yeddou, et al., 2009), tamarind seeds (Munusamy, et al., 2011) and many other materials such as apple pulp, cane bagesse, corn cob, date pits, eucalyptus wood, guava seeds, oat hulls, pea nut hulls, pecan shell, pine wood, rice husk, rice straw, rock rose and saw dust.

These materials were pyrolysed or carbobinized in an inert atmosphere in order to remove volatile organic constituents, leaving behind a highly porous carbonaceous residue, followed by either chemicals or physical activation at a presence of Nitrogin, Steam or Carbon dioxide to rise the pores in the char (Carbonized Material).

The preparation of activated carbons generally comprises two steps, the first is the carbonization of a raw material or precursor and the second is the carbon activation. The carbonization consists of a thermal decomposition of raw materials, eliminating non-carbon species and producing a fixed carbon mass with a rudimentary pore structure (very small and closed pores are created during this step). On the other hand, the purpose of activation is to enlarge the diameters of the small pores and to create new pores and it can be carried out by chemical or physical means. (Hernández-Montoy, et al., 2012)

2.4.1 Carbonization

Is a process by which solid residues with increasing content of the element carbon are formed from organic material usually by pyrolysis in an inert atmosphere. As with all pyrolytic reactions, carbonization is a complex process in which many reactions take place in parallel such as dehydrogenation, condensation, hydrogen transfer and isomerization. It differs from coalification in that its reaction rate is faster by many orders of magnitude. The final pyrolysis temperature applied controls the degree of carbonization and the residual content of foreign elements, e.g. at T = 730 ^{o}C the carbon content of the residue exceeds a mass fraction of 90 wt.%, whereas at T = 1330 C more than 99 wt.% carbon is found. (IUPAC, 2012)

According to the literature, the pyrolysis of lignocelluloses materials as coconut shells, olive stones, walnut shells, etc., gives rise to three phases: the char, oils (tars) and gases. The relative amount of each phase is a function of parameters such as temperature of pyrolysis, nitrogen flow rate and heating rate. (Hernández-Montoy, et al., 2012), following are some researchers used ranges of temperatures and different procedures in carbonization of different materials;

Husseien, et al., (2007); carbonized barley straw at different temperature from 200 to 500 ºC for 1, 2, 3 hours in muffle furnace using closed stainless steel tubes with length of 12.5 cm and inner diameter 2.5 cm, the tube had a hole in the top for venting gases produced during carbonization process.

Gueu, et al., (2006); carbonized the coconut shell and seed shell of palm tree by mixing with 35 ml of concentrated phosphoric acid and heating the mixture to 300 ^{o}C for 16 hrs.

Foo, et al., (Dec-2011); performed carbonization for Coconut husk by loading 500 g of dried precursor into a vertical furnace, and heated up to a carbonization temperature of 700 ◦C under purified N2 flow (150 cm3/min) while (Cruz, et al., 2012) carbonize the coconut husk at different temperatures 500, 650 and 800°C.

Mart´ınez, et al., (2005); dried Walnut shells at 100 °C, and ground with a roller mill to obtain samples of 1–3 mm particle size. The samples were carbonized separately in a muffle furnace heated from room temperature to 600 °C (1 h) under a constant flowing nitrogen atmosphere.

The researchers who used the olives seeds as the raw materials, has used different tempratures for carbonization which affect the charactraistcs of the produced activiated carbon.

Aljundi, et al., (2008); Four samples of olive cake were studied. Three of them were carbonized by heating the samples to 500 °C (5.5 8C/min) in 60 mL/min N $_{2}$ for 1 h, thereafter the samples were activated by flowing 50 mL/min CO_2 through the bed at 500 °C (AC500), 600 °C (AC600), and 700 °C (AC700).

El-Hamouz, et al., (2006); carbonized the Olives by placing it in a pre-cleaned dry clay dish and placed inside a tube furnace under nitrogen atmosphere. Heating was started from room temperature with a high ram rate (above 20 °C/ min) reaching a steady temperature of 500 °C where heating continued for 20 min under nitrogen flow.

El-Sheikh, et al., (2003); took 30 g of olive stones and crushed it with hammer, ground it using a mill and then dried at 120 °C overnight. Carbonization took place in a horizontal tube furnace heated from room temperature to 850 °C at 20 °C under a constant flowing N_2 atmosphere.

Moreno-Castilla, et al., (2000); Carbonize olives solid in a furnace at 350°C for 1 h under air flow (300 cm^3/min)

Demiral Hakan, et al., (2011); Carbonize the olives bagasse after sieving the crushed seed to 0.425-0.6 mm size, drying and placing it in a horizontal steel tube placed in a tube furnace and heated in nitrogen flow (150 cm3/min) from room temperature to a constant 500 °C.

2.4.2 Activation

Physical activation the reaction occurs between carbon atom and the oxidizing gas. Where the reaction increases the pore creation and development as some parts of the char structure are reacted faster. “During this reaction if carbon atoms were to be removed from the interior of incipient pores formed as a result of devolatilization during carbonization enlargement of opened micro-pores and the opening up of the closed micro-pores takes place If the burn off were to be from outside of the particle no new porosity results but it facilitates the reduction of particle size”. (Viswanathan, et al., 2009). Physical activation is considered as an environmentally friend as the activation need gaseous agents and there is no wastewater produced in this method. However, still some disadvantages can be considered in this method. It need long time and high energy consumable to produce microporous activated carbon. In addition, the yield of this method is not high as a large amount of the carbon mass is eliminated to produce a well developed pore structure of the activated carbon. (Viswanathan, et al., 2009)

Chemical activation, this method need a chemical activating agent like acids or alkali to activate the char. “The activating agents employed function as dehydrating agents that influence pyrolytic decomposition inhibiting the formation of tar and thereby enhancing the yield of carbon” (Viswanathan, et al., 2009). Usually the needed temperatures in chemical activation are lower than needed for physical activation. Therefore, the resulted porous structure is better in chemical activation. In the other side chemical method has some disadvantages such as the amount of wastewater needed it to wash the product in order to remove the residual inorganic material which may has a bad impact on the environment and need to control the pollution may resulted. (Viswanathan, et al., 2009).

Following are some different procedures used by researches to activate carbon;

Alau, et al., (2010): used three different chemicals H_3PO_4, KOH and $ZnCl_2$g to activate Neem husk, in producing activated carbon. The researcher found that Neem husk is effective in removing of organic reagent such as xylenol orange, dyes such as procion red and remazol turqoise blue once these chemical activates it. When comparing the activated carbon with the commercial ones it showed that adsorbent from coconut shell for the adsorption of the above materials is favorable.

Foo, et al., (2011); the researcher activated the Coconut husk by adding and mixing the char with different activation agents (H_2SO_4, H_3PO_4, HNO_3, K_2CO_3, NaOH and KOH). The impregnation ratio (dry weight of activation agent / weight of char), and the type of the agent has been checked in the study. The experiment steps started by locating the impregnation in a glass reactor fixed in the chamber of microwave oven connected to Nitrogen gas with a flow rate (300 cm^3/min) to purge air in the reactor before the start of microwave heating and continued to flow through activation. The study showed that Potassium hydroxide appears to be a better activation agent in terms of both adsorption capacity and carbon yield in addition to microwave-assisted activation has successfully reduced the heating period, which represents the reduction of energy and cost as well,

Mart´ınez, et al., (2005); has used Chemical activation to activate the char of Walnut shells and Olives stones using potassium hydroxide with two different concentrations (50 and 75%, w/w), at a ratio of 1:1 (KOH solution/char, w/w). After the char was mixed with the KOH solution, the mixture was dried at 300 °C for 3 h and immediately activated at 900 °C in inert atmosphere (Nitrogen) for 1 h. the study shows that KOH concentration used for activation and particle size of the carbons obtained can modify the adsorption capacity of the products.

Aljundi, et al., (2008); has activated the char of the olive cake by flowing 50 mL/min CO_2 at 500 °C through the reactor at different temperatures 600 and 700 °C. This study showed that olive cake could be used as a source for production of activated carbon suitable for removing iron metals. In addition to a combination between chemical and physical activation will improve the resulted adsorption capacity through increasing surface area and pore volume. In addition, physical activation using CO_2 alone will produce low surface area when activation temperature is below 700 °C.

Moreno-Castilla, et al., (2000); has carbonize the Olive char in a furnace at 350°C for 1 h under air flow and activate the char with KOH. In the experiments, different KOH/char mass ration has been investigated while drying and treating it with N_2 at 300 °C for 3 hours is the same. In addition, H_3PO_4 is used for activation with different mass ratios and same heating temperature 500 °C for one hour. The obtained results shows that chemical activation of olive-mill with KOH produced activated carbons with low ash content, higher surface area and better developed porosity than in chemical activation with H_3PO_4 and physical activation with CO_2 at 840 °C.

Demiral Hakan, et al., (2011); in the activation of olive bagasse the resulted char was heated from room temperature to (750, 800, 850 and 900 °C) under nitrogen flow (20 cm^3/min) with a heating rate of 10 °C/min, when the activation temperature was reached, nitrogen flow was switched to steam. In steam activation, water vapor flow was provided by injection of 0.08 ml/min (measured at room temperature) of liquid water to hot reactor by a peristaltic pump. The results of this research shows that activated carbon prepared by physical activation achieved a maximum value of 1106 m^2/g at activation temperature of 900 °C with activation time of 45 min.

Microwave activation

Microwave heating is used for material processing that includes drying of materials, treatment of coal, and regeneration of adsorbents. Microwave heating compared to conventional heating has many advantages because of its fast heating rate, high energy efficiency, and the selective and volumetric nature of the heating where the heat flux is from the inside to the outside of the heated material. Carbonaceous material, such as graphite flakes, carbon black, carbon fibers and filaments and activated carbon, can be heated with microwaves because of the semi-conductivity of carbon. (Chen, et al., 2012).

Deng, et al., (2008); investigated the activation of the carbon produced from cotton stalk with $ZnCl_2$ under microwave radiation. Different microwave power, microwave radiation time and the impregnation ratio of $ZnCl_2$ factors has been evaluated on the yield and adsorption capacities of activated carbon. The results indicated that: microwave power of 560 W, microwave radiation time of 9 min. and the impregnation ratio of $ZnCl_2$ was 1.6 g/g are the optimum conditions to produce Activated carbon from cotton stalk.

Deng, et al., (2010); cotton stalk was used to produce activated carbons, the activation performed using different activation agents (KOH and K_2CO_3) and under different microwave radiation. The results of the study showed that KOH created a greater micro pore volume than K_2CO_3 did. Microwave heating when compare it with conventional heating method, microwave could shorten the activation time and reduce the consumption of KOH.

Liu, et al., (2009); activated carbon from Bamboo was prepared with a microwave activation process at presence of activating agent as phosphoric acid. Different factors such as radiation time, phosphoric acid/carbon ratio and microwave power, were studied on the activation results. Activation conditions of; microwave power 350 W, radiation time 20 min and phosphoric acid/carbon ratio 1:1 were the optimal conditions, which gave a surface area of 1432 m^2/g and a carbon yield of 48%.

Li, et al., (2007); tobacco stems was used to produce activated carbons, K_2CO_3 used for activation through microwave radiation, time of radiation and Effects and K_2CO_3/C ratios are investigated on the yield and adsorption capacities of activated carbons. Results showed that the optimum conditions for producing activated carbon from

Tobacco stems were as follow: microwave radiation time 30 min, microwave power 700 W, and K_2CO_3/C ratio 1.5.

Foo, et al., (Feb-2011); through this study a low cost activated carbon was prepared from date stones char using microwave heating in addition to KOH. The activation process was executed at the 600 W microwave input power and 8 min irradiation time. The produced activated carbon has a total pore volume and a surface area as 0.4680 cm^3/g and 856.23 m^2/g, respectively.

Foo, et al., (May-2011); used pistachio nutshell to produce activated carbon by microwave heating with KOH addition. Activation was performed at 600 W input power and time of irradiation is 7 min. the results showed that the BET surface area was 700.53 m^2/g, Langmuir surface area was 1038.78 m^2/g, and total pore volume was 0.375 /g , respectively.

Yagmur, et al., (2008); The tea waste used to produce activated carbon by adding phosphoric acid for activation through microwave heating treatment and with conventional heating, carbonization occurred under nitrogen atmosphere at various temperatures and different phosphoric acid/precursor mixture ratios. The properties of the activated carbons were tested by elemental analysis. The maximum BET surface area was 1157 m^2/g for the sample treated with microwave heating and then carbonized at 350 ^oC. and for the conventional method, the BET surface area of the resulted activated carbon was 928.8 m^2/g at the same conditions.

2.5 Adsorption

Adsorption is the process by which molecules of a substance (Adsorbate), such as a gas or a liquid, collect on and adhere to the surface of another substance (Adsorbent), such as a solid. The molecules are attracted to the surface but do not enter the solid's minute spaces as in absorption. Adsorption may occur at the outer surface of the adsorbent and in the macro-pores, meso-pores and micro-pores in the inner cracks of the adsorbent (Rabah, 2010).

There are many forces that cause the adsorption is a combination of the following forces;

Van der waals force: “ The attractive or repulsive forces between molecular entities (or between groups within the same molecular entity) other than those due to bond formation or to the electrostatic interaction of ions or of ionic groups with one another or with neutral molecules. The term includes: dipole–dipole, dipole-induced dipole and London (instantaneous induced dipole-induced dipole) forces. The term is sometimes used loosely for the totality of nonspecific attractive or repulsive intermolecular forces” (IUPAC, 2012).

Hydrogen bonds: “A form of association between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges” (IUPAC, 2012).

Steric interaction (effect): “arise from the fact that each atom within a molecule occupies a certain amount of space. If atoms are brought too close together, there is an associated cost in energy due to overlapping electron clouds (Pauli or Born repulsion), and this may affect the molecule's preferred shape (conformation) and reactivity” (Farlex, 2013).

Hydrophobicity: “is the association of non-polar groups or molecules in an aqueous environment which arises from the tendency of water to exclude non-polar molecules” (IUPAC, 2012).

2.5.1 Factors affecting Adsorption

Many factors are affecting adsorption such as; characteristics of adsorbent, Ho, et al., (2001), Solubility of adsorbent, size of Adsorbate molecules, Temperature, contact time and pH.

As particle, size of the Adsorbate increases the rate of adsorption decreases and this is clear as powder Activated Carbon (PAC) has a higher rate than the Granular Activated Carbon (GAC). This is proved by Bla´zquez, et al., (2004), where the study shows that the percentage removal of the Cadmium drop from 90% to 75% when the particle size increased from 0.35 mm to more than 1.0 mm. The study of removing Lead(II) by Ho, et al., (2001); shows that an increase in the rate sorption as the mean diameter of the peat decreases.

pH is considered as a major factor affecting the sorption of metals, according to many studies, pH is changing the characteristics and the availability of ions in the solution (Bla´zquez, et al., 2004). For Cadmium removal by Olive stone the study of Bla´zquez showed that as the pH increased the percentage removal is increased from 45% at pH 3 to 90% at pH 11. Gueu, et al., (2006) study show that the sorption capacity of removal zinc by activated carbon prepared from coconut shells at pH < 3 is low while from 3 to 5 it increases rapidly and small increase in sorption capacity with a high change in pH.

Ho, et al., (2001); study the effect of temperature in removing Lead(II) by activated carbon which prepared from peat, the study shows that for a constant time, the increase in temperature increases the sorption capacity and after a certain time 150 minutes the sorption capacity almost the same, meanwhile the effect of agitation (revolution/minutes) is not significant but still the increase in agitation is increasing the sorption of lead (II).

In most of the experiments to test the effect of the contact time, it is clear that to a certain time which is called equilibrium time the adsorption continues in a high rate, until equilibrium occurs and it slow down almost to zero, time to reach equilibrium depends on the adsorbate and the absorbent.

Following Figure 2-5 is the effect of contact time in removing heavy metals by adsorption:

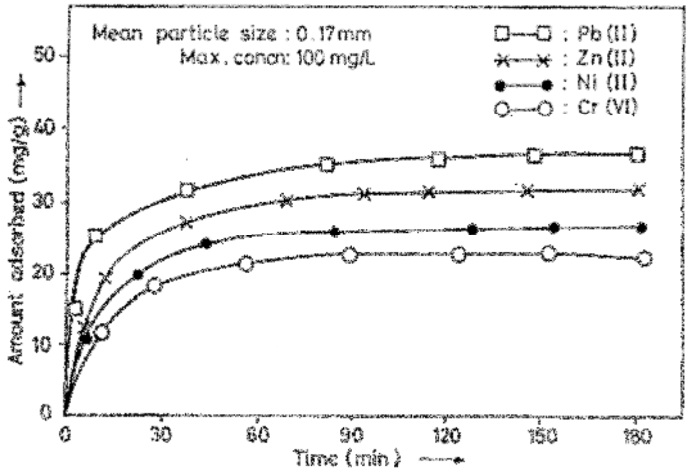


Figure 2-5 Effect of contact time on adsorption of heavy metals ((Saravanane, et al., 2001)

2.5.2 Treatment by Adsorption

To meet today’s high quality water and wastewater standards, Adsorption is a fundamental process in the physicochemical treatment of water and municipal wastewaters. Through adsorption treatment a higher effluent standards can be achieved with low cost at water treatment facilities for drinking water, in addition to good effluent of wastewater treatment plants, that can be reused in many fields such as industrial and agricultural fields.

Through this literature review, many references have been included in which researches show the removal of many metals and contaminants from either drinking water or wastewater by adsorption treatment such as Cadmium, Zinc, Lead, COD, Sodium Dodecyl Sulfate, Ammonia and cyanide and many other materials.

Chemicals can be classified by the probability of efficiency of being adsorbed as shown in Table 2.4 and the previous discussed factors and the type of the activated carbon affect this efficiency. By experiments equations (Adsorption Isotherms) has been developed to determine the amount of materials adsorbed, the most famous isotherms are : Freundlich isotherm and Langmuir isotherm

Table 2.4: Probability of being efficiently adsorbed by activated Carbon.

very high probability		**high probability**	**moderate probability**	**unlikely to be effective**
2,4-D	Bromacil	Aniline	Acetic acid	Acetone
Deisopropyltatrazine	2,4-Dichlorophenoxy	Dibromo-3-chloropropane	Dimethoate	Methylene chloride
Linuron	Nitrobenzene	1-Pentanol	Methionine	Acetonitrile
Alachlor	Bromodichloromethane	Benzene	Acrylamide	1-Propanol
Desethylatrazine	Dieldrin	Dibromochloromethane	Ethyl acetate	Acrylonitrile
Malathion	m-Nitrophenol	Phenol	Methyl-tert-butyl ether	Propionitrile
Aldrin	p-Bromophenol	Benzyl alcohol	Chloroethane	Dimethylformaldehyde
Demeton-O	Diethylphthalate	1,1-Dichloroethylene	Ethyl ether	Propylene
MCPA	o-Nitrophenol	Phenylalanine	Methyl ethyl ketone	1,4-Dioxane
Anthracene	Butylbenzene	Benzoic acid	Chloroform	Tetrahydrofuran
Di-n-butylphthalate	2,4-Dinitrocresol	cis-1,2- Dichloroethylene	Freon 11	Isopropyl alcohol
Mecoprop	p-Nitrophenol	o-Phthalic acid	Pyridine	Urea
Atrazine	Calcium Hypochloryte	Bis(2-chloroethyl) ether	1,1-Dichloroethane	Methyl chloride
1,2-Dichlorobenzene	2,4-Dinitrotoluene	trans-1,2-Dichloroethylene	Freon 113	
Metazachlor	Ozone	Styrene	1,1,2-Trichloroethane	
Azinphos-ethyl	Carbofuran	Bromodichloromethane	1,2-Dichloroethane	
1,3-Dichlorobenzene	2,6-Dinitrotoluene	1,2-Dichloropropane	Freon 12	
2-Methyl benzenamine	Parathion	1,1,2,2-Tetrachloroethane	Vinyl chloride	

very high probability		high probability	moderate probability	unlikely to be effective
Bentazone	Chlorine	Bromoform	1,3-Dichloropropene	
1,4-Dichlorobenzene	Diuron	Ethylene	Glyphosate	
Methyl naphthalene	Pentachlorophenol	Toluene	Dikegulac	
Biphenil	Chlorine dioxide	Carbon tetrachloride	Imazypur	
2,4-Dichlorocresol	Endosulfan	Hydroquinone		
2-Methylbutane	Propazine	1,1,1-Trichloroethane		
2,2-Bipyridine	Chlorobenzene	1-Chloropropane		
2,5-Dichlorophenol	Endrin	Methyl Isobutyl Ketone		
Monuron	Simazine	Trichloroethylene		
Bis(2-Ethylhexyl)Phthalate	4-Chloro-2-nitrotoluene	Chlorotoluron		
3,6-Dichlorophenol	Ethylbenzene	4-Methylbenzenamine		
Napthalene	Terbutryn	Vinyl acetate		
m-Xylene	2-Chlorophenol			
Cyanazine	Hezachlorobenzene			
Isooctane	Tetrachloroethylene			
o-Xylene	Chlorotoluene			
Cyclohexane	Hezachlorobutadiene			
Isoproturon	Triclopyr			
p-Xylene	Chrysene			
DDT	Hexane			
Lindane	1,3,5-Trimethylbenzene			
2,4-Xylenol	m-Cresol			
Isodrin				

2.6 Measurements

Through this section, a standard method of measuring the main indicators or characteristics of the materials will be illustrated as described by international standards, except where indicated when using an approximate method because of shortage of materials or equipments in The Gaza Strip strip.

It is important to indicate that through all the measurements in the research three replicates for each experiment has been done and the results are the average of these three replicates.

2.6.1 Characteristics of Activated Carbon

Activated carbon is characterized by its physical properties and the activity properties, and both are very important factors in specification of any prepared carbon. Important ***physical properties*** are surface area, product density; mesh size, abrasion resistance and ash content.

Due to its high degree of micro porosity, just one gram of activated carbon has a surface area in excess of 500 m^2, as determined by adsorption isotherms of carbon dioxide gas at room or 0.0 °C temperature.

In water treatment applications, carbon density is expressed as back washed and drained or bulk density. This establishes the number of pounds of carbon required to fill a back washable filter, and is expressed in terms of pounds per cubic foot.

Particle size is an important parameter in specifying carbons for specific applications, affecting such operating conditions as pressure drop, filtration capabilities, backwash rate requirements and the rate of adsorption of contaminants.

Another important characteristic that distinguishes different types of liquid phase carbons is abrasion resistance. Abrasion resistance refers to a carbon's ability to withstand degradation during handling and is expressed in terms of abrasion number.

Activity characterizations are key indicators of a carbon's potential performance for removing contaminants from water. An important characterization tool used in determining the ability of a carbon to adsorb a particular adsorbent is the pore size distribution. The pore size distribution is produced through adsorption of gases and liquids under pressure. It defines the available pore volume of a carbon over three pore size regions (macro-pores, meso-pores and micro-pores).

Through this study part of the carbon characteristics will be determined through experiments and following are the standard method used for measuring these characteristics, while in some characteristics an approximate method is used because of shortage of equipments in The Gaza Strip, the method used will be explained in the next chapter.

2.6.1.1 Activated Carbon Surface Area

The commonly known standard method of measuring the surface area as per the (Deutsches Institut für Normung) DIN 66131 BET and the new version of the standard (DI ISO 9277 (2003-05), and the ASTM D-4820-99.

"The surface area is measured by evaluating the amount of nitrogen absorbed, at liquid nitrogen temperature, by a carbon black standard (or other carbon black sample) at several (at least five) partial pressures of nitrogen". (ASTM, 1999).

A complete procedure is included in Appendix B.

Because of shortage of equipments in The Gaza Strip and other countries, in addition to the high cost of the test, and safety requirements and assuming a mono-layer coverage according to Langmuir Isotherm an approximate testing method is available using the **acetic *acid Isotherm test***, and can be summarized into the following steps: (The test used in the study). The test is described and used in the reference research (El-Hamouz, et al., 2006) refernced from (Glasstone and Lewis, 1983; Richard and Marilyn, 2004),

1. Activated carbon was washed several times with distilled water and dried at 120°C till constant weight is reached.
2. Seven glass bottles were treated by acetic acid (0.5 M), for 60 minutes, and after that rinsed with water and dried with compressed air.
3. Taking seven samples of the activated carbon each weighted 1 gram and placed it into the pretreated bottles.
4. A range of acetic acid concentrations was prepared between C_o 0.015 to 0.15 M each 100 ml and place it into the bottles where the activated carbon was placed.
5. At a 25 °C the bottles are kept and periodically shaking the bottles for 60 minutes until reach equilibrium.
6. Filter the samples and eliminate the first 10 ml and titrate using NaOH 0.1 M and Phenolphthalein,
7. measure the number of moles adsorbed at equilibrium for all the samples C_e , and calculate the total number of moles adsorbed per gram of activated carbon $N = (C_o - C_e)*V/g$ (V: volume of samples, g grams of activated carbon, C_o : Initial Concentration, C_e : Final Concentration at equilibrium).
8. A graph is plot for C_e Vs C_e/N, according to the equation $C_e/N= C_e/N_m +1/k_LN_m$ $1/N_m$ is the slope of the curve is giving the number of acetic acid moles adsorbed

by a gram of activated carbon, $1/K_L$ is a constant equal the intersection from the Y axis as shown in Figure 2-6

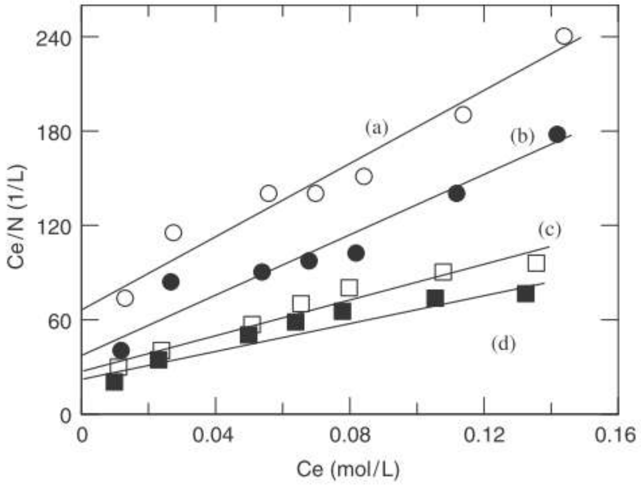


Figure 2-6 Langmuir plots for acetic acid adsorption onto AC with different particle sizes (El-Hamouz, et al., 2006)

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

2.6.1.2 Bulk Density (CEFIC, April 86)

Bulk density is the mass of the unit volume of the sample in air, including the pores and the voids between the particles and expresses as kg/m^3. Bulk density depends on the shape and the size of the activated carbon and the density of the individuals' particles.

The value of the bulk density is important in estimated the tank bulk volume, the standard method for measuring the bulk density are as specified in DIN ISO 787,11 and ASTM D 2854. And can be summarize as following:

1. A dry sample is prepared after drying it in an oven to reach constant weight,

2. In a graduated cylinder fixed in a vertical tapping device with a frequency 250 +/- 15 taps/min amplitude 3 mm, a 200 ml of activated carbon is placed avoiding entraining air.

3. The top is flatten and the cylinder onto the machine and cycle 1250 times, the volume is read.

4. The procedure is repeated until the difference between the two observation is less than 2 ml. (V)

5. The weight of the content of the cylinder to the nearest 0.10 g (M)

6. Bulk density $D_b = 1000\ M/V$

2.6.1.3 Ash Content (CEFIC, April 86)

Ash content is the measuring of the residual materials left behind the carbonization and activation and the increase of the ash content the less efficient of the activated carbon will be. Ash content can be measured as per ASTM D 2866-70 as following:

1. Dry an adequate sample of activated carbon to a constant weight at 150 ^{o}C Minimum three hours.

2. Ignite the crucible in the muffle furnace at 650 ^{o}C for 1 hour, cool to room temperature and weight the crucible (G) grams

3. Place a sufficient amount of dried activated carbon and weight both the activated carbon and the crucible to nearest 0.1 g (F).

4. Place the content (crucible and activated carbon) in the furnace at 650 ^{o}C to ash the content, it may take from 3 to 16 hours, till constant weight is reached (B).

5. Ash content is given by $A_c = 100\ (B\text{-}G)/(F\text{-}G)$

2.6.2 Detergent/Surfactant concentration: MBAS (Methylene Blue Active Substances)

The standard method for measuring the detergent and mainly the Ionic surfactant is MBAS (Methylene Blue Active Substances), where the intensity of the resulting blue color in the organic phase is measured.

As per Standard methods for the examination of water and wastewater 19th edition, section 5540C , the experiment can be summarized into the following steps:

1. Preparation of Calibration curve, where a series of different concentration of standard LAS (Linear alkylbenzene sulfonate) is used and a full process of Ion pairing and extraction as following:
    a. Making the sample alkaline by dropwise addition 1N NaOH using phenolphthalein indicator, and discharging pink color by dropwise addition of 1N H_2SO_4.
    b. Peroxide treatment, to avoid decolorization of the methylene blue by sulfide, a few drops of 30% H_2O_2 may added.
    c. Addition of 10 ml $CHCl_3$ and 25 ml Methylene blue reagent , and shake in a separatory funnel.
    d. Draw of the layer of $CHCL_3$ in another separatory funnel, rinsing delivary tube of the first separatory funnel with a small amount of $CHCl_3$ and repeat extraction two additional times using 10 ml $CHCl_3$ each time.
    e. Combining all $CHCl_3$ extracts in the second separatory funnel, and adding 50 ml wash solution and shaking for 30 seconds. Letting it settle and drawing off t$CHCl_3$ layer through a funnel containing a plug of glass wool into a 100 ml volumetric flask.
    f. Extract wash solution twice with 10 ml $CHCl_3$ each and add to flask through a glass wool and collect the rinse of the glass wool and the funnel with $CHCl_3$ and dilute to mark with $CHCl_3$ and mix well.
2. Measuring the absorbance at 652 nm against blank of $CHCl_3$
3. Sample size, based on the expected MBAS concentration the sample is taken as following (0.025-0.08 mg/l taking 400 ml, 0.08-0.40mg/l taking 250 ml, and 0.4-2.0 mg/l taking 100 ml) and if MBAS concentration is more than 2mg/l the sample can be diluted with water.

4. Peroxide treatment, to avoid decolorization of the methylene blue by sulfide, a few drops of 30% H_2O_2 may added.

5. Same procedure done step 1 should be repeated for the samples followed by step No 2 for measuring the absorbance

6. For calculation, from the calibration curve the micrograms of apparent LAS (mol wt ---) corresponding to measured absorbance :

$$\text{mg MBAS/L} = \mu\text{g apparent LAS / mL original Sample}$$

CHAPTER 3: RESEARCH METHODOLOGY

The methodology of this research is based on the experimental procedure for investigating the possibility of removing detergents from wastewater, and will be divided into two parts:

- Producing activated carbon from crushed seeds and find out its important characteristics.
- Investigating the possibility of removing detergent from aqueous solution and run the experiment on samples collected from local wastewater treated plants.

3.1 Producing activated carbon

3.1.1 Samples collection

There are 18 olive mills in The Gaza Strip strip (PCBC, 2012), where the harvested olives transported and olive oil is produced. The solid waste collected at back yard of the olive mill as shown in Figure 3-1. The season of olives harvesting start late September but producing olives oil start late October to end of November every year, the samples were collected from Gaza city (Yafa Street Olive mill), fresh samples were collected directly at the outlet of the grinding machine, following Figure 3-1 show the site:

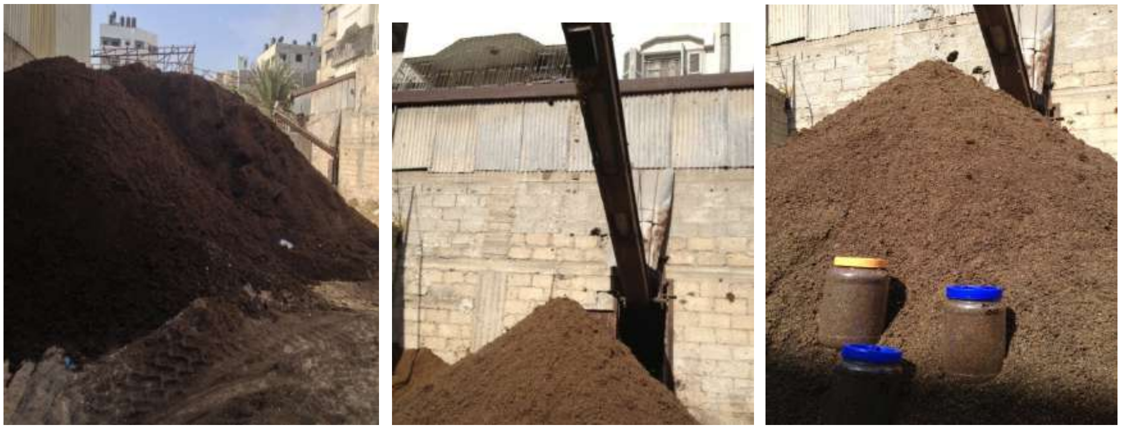


Figure 3-1:Olive Seeds, Samples collection

Samples have been taken to the lab, cleaned very well from dust by washing it with distilled water. The crushed seeds have been separated from the grinded leaves and pomace through floating it in water, where the seeds settle and the other parts float and scraped until the crushed seeds is clean as shown in the Figure 3-2 below:

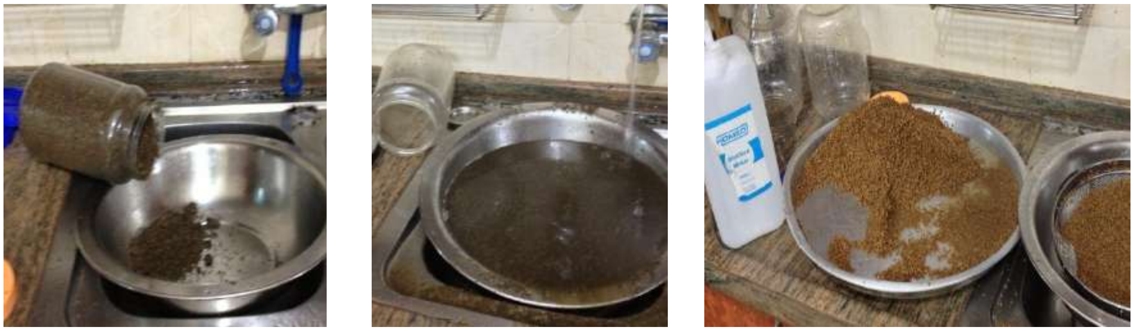


Figure 3-2: Cleaning and Preparation of Crushed Olive Seeds

The samples dried in an oven for 24 hours at a temperature of 105 °C and sieved. The collected samples between 1-2 mm were taken a side and the larger was crushed and sieved to the same size. The collected samples are stored in a very well closed glass jar until use.

3.1.2 Carbonization of the Olive seeds

Following the same literature of (Aljundi, et al., 2008) and (Demiral, et al., 2011) for carbonization of the olive stones at a temperature of more than 500 °C with a constant flow of Nitrogen.

This stage started by searching for a muffle furnace in the Gaza strip with an access to allow Nitrogen to flow inside the furnace. Only one muffle furnace found in Gaza Educational Center (UNRWA) and they refused to do any modification with it to allow nitrogen gas flow inside the furnace or locate a reactor inside the furnace therefore, the decision is taken to manufacture the oven and the reactor.

An ordinary home oven used for bakery with a certain modification requested from the manufacture to allow the thermal isolation for all sides of the oven has been chosen. The walls and roof of the oven has been covered with y-tong bricks 5 cm thick and fixed to walls, roof, and bottom with bolts as shown in the following Figure 3-3:

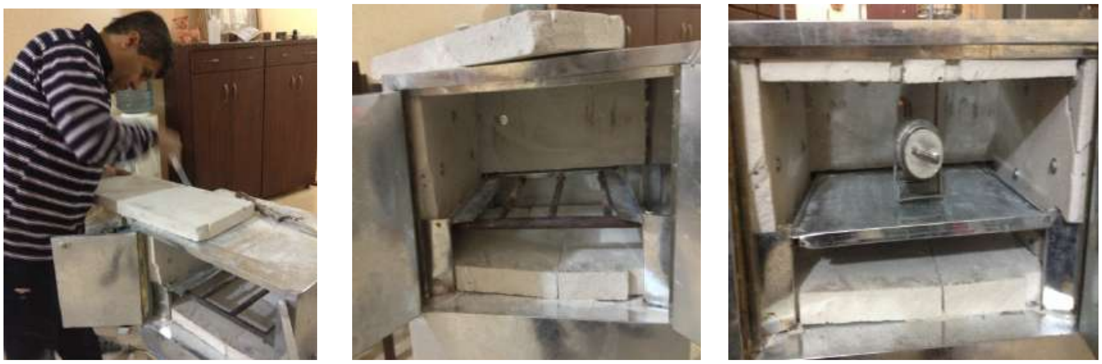


Figure 3-3: Manufacturing the oven and reactor

The oven is equipped with a thermometer graded from zero temp to 550 ^{o}C fixed from the top of the oven through a small hall right touching the rector. The reactor is made from a stainless steel tube 7.5 cm diameter, 20 cm length, with a threaded closing cap, two 6 mm stainless steel pipes connected to it to allow nitrogen enter the reactor and the burned gases out of the reactor.

The Oven tested for reaching the required temperature, and after many trials for choosing the opening to allow air entering the oven and keep it burning in addition to prevent heat from loosing.

Oven has been prepared by connecting the cooking Gas and tested, the reactor located in the oven and connected to the Nitrogen source (10 liter capacity at 150 bar pressure) through a flow meter range from 0 to 25 liter/ minute as shown below Figure 3-4.

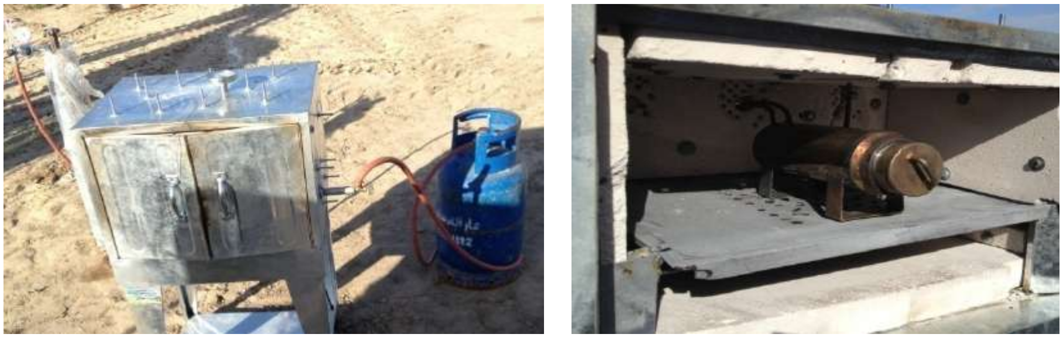


Figure 3-4: Oven and reactor arrangement

Carbonization of the olive seeds started by filling a 100 gram in the pan and inset it in the reactor, then start flowing Nitrogen through the reactor with 300-500 cm^3/minute. A few seconds when nitrogen start going out of the reactor heating started from room temperature with an increasing rate (about 40 ^{o}C/min) until reaching a steady temperature of 500 ^{o}C (Demiral, et al., 2011) and heating continued for 20 min under nitrogen flow with the same rate.

After Carbonization, as shown in Figure 3-5 all the quantity has been sieved and the size of 0.6 to 1.00 mm is taken as the targeted size (results of Bla´zquez, et al., 2004). Larger sizes have been crushed by a hammer and sieved to the targeted size. Smaller sizes such as 0.3 to 0.6 mm and o.15 to 0.3 and less than 0.15 mm has been collected for future tests.

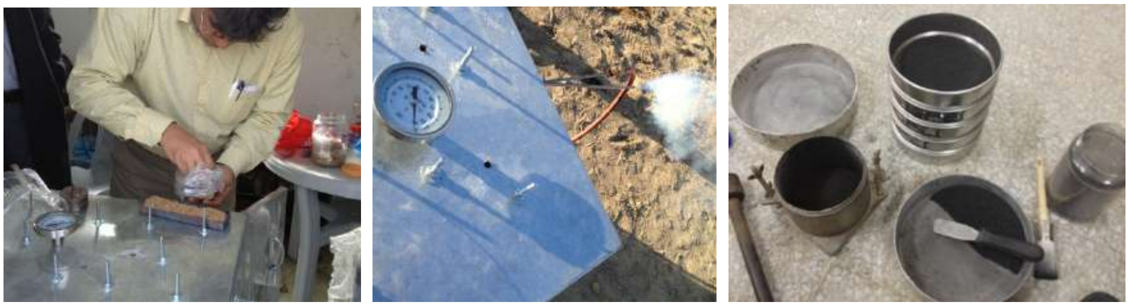


Figure 3-5: Carbonization process

Through carbonization, the following points were recorded:

1. Control the flow of nitrogen with a range 300 to 500 cm3/min, refers to the grading of the flow meter, which ranges from 1 liter/min to 25 liter/min and difficulty to have a fixed flow rate as per literature .
2. Control of temperature was difficult to have it less than the rate of 35 ^{o}C/min as the oven is a gaseous energy source not electrical.
3. After 5 minutes (from start) at temperature 200 ^{o}C steam start going out of the sample and drops of water is noticed.
4. After 12 minutes (from Start) Almost at 500^{o}C the smoking start released from the outlet, and drops of tar (Black viscous) came out of the outlet tube.
5. Smoking continued for 8 to 10 minutes and stop after that.
6. Another 10 minutes without any smoke at 500 ^{o}C has been continues.

3.1.3 Yield of Char

Three samples 100 g each from seeds which are cleaned and dried for 24 hours at 115 ^{o}C are taken to measure the yielding of carbonization, carefully after located inside the rector and the oven and the whole process is completed and cooled to room temperature, the resulted samples are weighted by electronic balance and recorded for calculating the yield.

3.1.4 Activation of the char

As discussed in the literature review, there are different ways of activation, chemical, physical and microwave. Every proceedure has its advantages and disadvantages as explained before, the activation by microwave and using a chemical activation agent such as KOH used by (Mart´ınez, et al., 2005), (Deng, et al., 2010) and (Foo, et al., May-2011), (Moreno-Castilla, et al., 2000) is found the least power consumption and high yielding, in addition to that " microwave heats the samples from the inside, which can create a temperature gradient that reduces gradually from the center to the surface of the samples. Due to this temperature gradient, the light components are released easily, which create more pores" (Moreno-Castilla, et al., 2000).

following are the steps of activation:

- Preparation of the microwave reactor: Different containers has been tested to find out the ability to stand inside the microwave with chemicals and high temperature such as ordinary flask, pyrex flask, clay dishes, the results was broken flask or container after 20 minutes, see Figure 3-6:

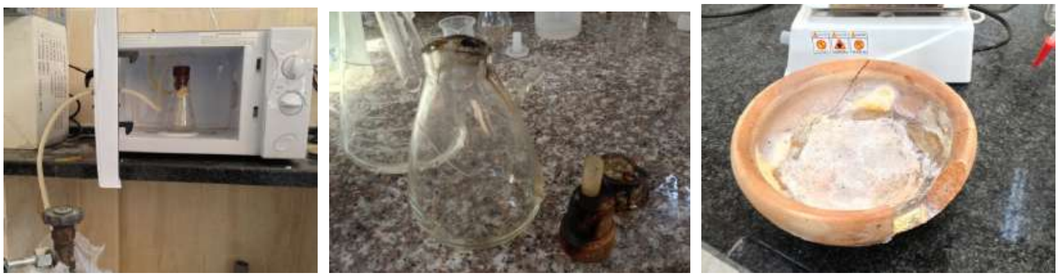


Figure 3-6: Reactor alternatives for activation

The final arrangement of the reactor used as shown in the following Figure 3-7 :

A (700 W, 2450 MHz, Durabrand XB2316, UK) microwave is selected with two holes one at the top and the other one at the side to allow the nitrogen enter the reactor.

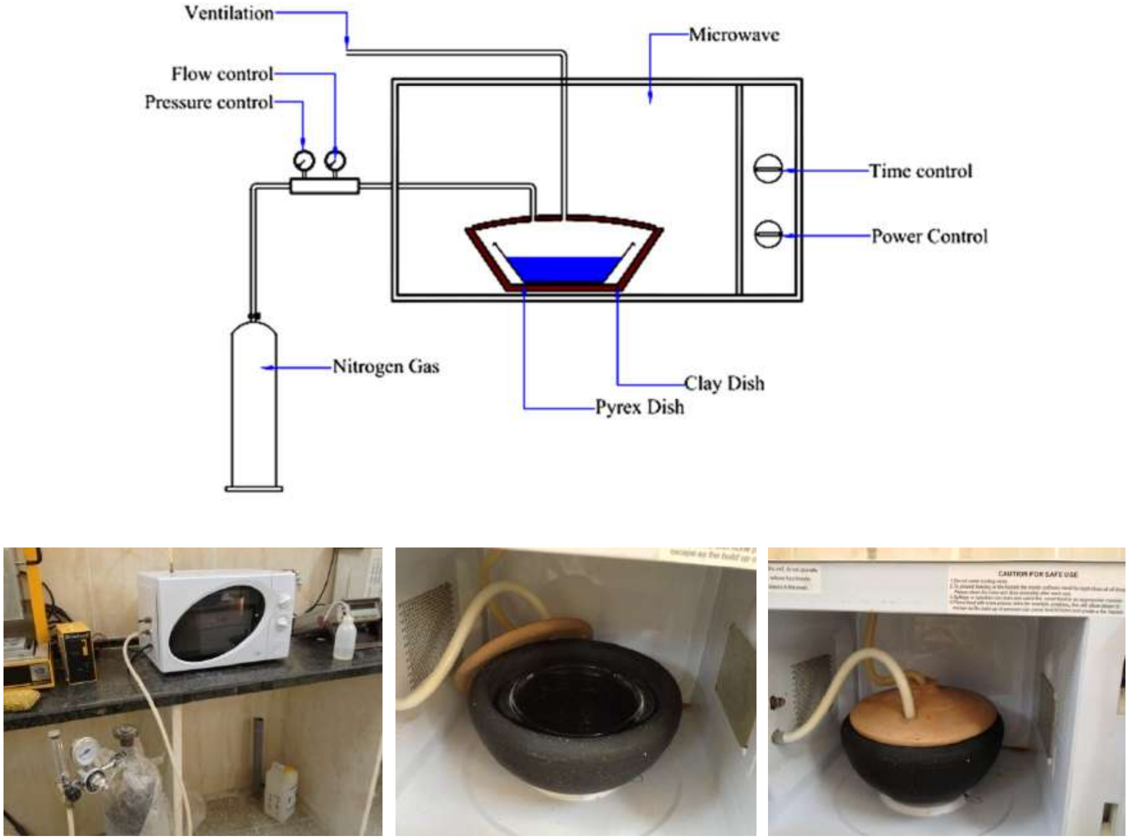


Figure 3-7: Equipments for Activation Process

The inlet pipe was connected with a flow meter and the nitrogen gas container.

The clay dish filled partially with water to the top level of the Pyrex dish which contains the carbon and the potassium Hydroxide 1:2 w/w , and potassium Hydroxide pellets is dissolved at 80 ml of distilled water (enough to cover the carbon).

The following points has been considered in all the activation process:

1. Char size chosen is 0.6 to 1.0 mm
2. Nitrogen flow ranges 300 to 500 ml/minute
3. Microwave power is 700 watt

4. Potassium Hydroxide KOH /Activated carbon ration is 2/1 w/w similar to the study performed by (Moreno-Castilla, et al., 2000)
5. No stoppage while doing activation
6. Carbon is located inside the pyrex dish and potassium hydroxide solution carefully poured on top of the carbon and mixed before inserted inside the microwave.
7. The cove closed as tight as possible and nitrogen flow checked coming out of the ventilation tube.
8. Time selected for activation is (5, 10, 15, 25, 35) minutes.
9. The samples left inside the microwave till cooling and nitrogen continue flowing all the time until the sample taken out of the microwave.
10. The samples are filtered and washed with clean water and distilled water until the cleaning water pH ranges from 7 to 7.5 and cleaning stopped.
11. The samples were dried in oven at 110 ^{o}C for 24 hours and stored.

Followings are difficulties faced at activation:

1. Control the flow rate of the nitrogen to a fixed figure was difficult, therefore a range is considered.
2. Failure in finding a closed container as a reactor that can stand in high temperature produced from the microwave without destroyed was very difficult and many alternatives were checked.
3. Because the reactor is not rotating inside the microwave, radiation noticed to be concentrated at one side of the reactor and this cause the damage to the rectors until the last configuration shown in Figure 3-7 where the whole equipments stand for the required durations.
4. Cleaning the activated carbon from the potassium hydroxide is taking a long time between cleaning and measuring the pH.

3.1.5 Characteristics of the produced Activated Carbon:

3.1.5.1 General appearance and texture

The produced activated carbon and the char from the previous steps have been taken under a microscope to show the difference between the surfaces of char and activated carbon. There is no Available Scanning Electronic Microscope (SEM) in Gaza Strip to show more details of the pores in the char and the produced activated carbon. By using Digital microscope type (Gentaur DN-200 M) connected by a camera to the computer at the laboratory of testing material (Mechanical Department) at Islamic University and using a portable concentrated lighting at the surface of the carbon particle clear photos have been taken to the char and the produced activated carbon.

The first photo is taken for the char with a enlarge of 200 times of original size and the same for the produced activated carbon, the third photo with a double enlargement 400 time the original size.

3.1.5.2 Surface area

As described in section 2.6.2.1 and shown in Appendix A the standard procedure for measuring the surface area is by Nitrogen adsorption, this procedure give more accurate results as the nitrogen adsorbed in one layer and penetrate inside all the pores. The Acetic acid procedure described in the literature review the same section and used by (El-Hamouz, et al., 2006) and previously by (Glasstone and Lewis, 1983; Richard and Marilyn, 2004) is used assuming a monolayer coverage, according to Langmuir isotherms. This procedure is used because it is cheaper and can be done in Gaza labs, while it is very difficult to arrange for Nitrogen adsorption test with a 70 K temperature (-196 ^{o}C).

Commercial Activated Carbon: The first experiment performed to measure the surface area of a commercial type with a well-known surface area measured by BET N_2 to test the performed procedure and find out the correction factor for the following measurements on the produced activated carbon. Following is in Table 3.1 the characteristics of the commercial activated carbon as described by the manufacturer (Jacobi Carbon – Aqua-Sorb 2000). The procedure of the experiment is as described in the literature review and the input and output data are shown in Table A.1.

Comparison between commercial carbon characteristics and produced carbon is shown at Table 4.4.

Table 3.1: Characteristics of Commercial Activated Carbon (Jacobi Carbon – Aqua-Sorb 2000)

Parameter	Unit	Value	Test Method
Iodine number	mg/g	1050	ASTM D4607
Surface area	m^2/g	1100	BET N_2
Methylene blue	mg/g	280	JACOBI T4001
Total pore volume	cm^3/g	1.04	Porosimetry(N_2/Hg)
Apparent density	Kg/m^3	470	ASTM D2854
Bed density, backwashed and drained	Kg/m^3	410	Note 1
Wettability	%	99.5	JACOBI T4003
Moisture content -as packed	%	2	ASTM D2867
Water soluble matter	%	0.2	ASTM D5029
pH		8	ASTM D3838
Chlorine half length value (12x40 USS)	cm	2.2	DIN 19603
Ball-pan hardness number	%	95	ASTM D3802
Note 1: Value is based on the backwashing of a bed of AquaSorb ® 2000 activated carbon at 30% expansion, which has been allowed to drain and settle.			

Surface area of produced activated Carbon

The selected char of sizes between 0.6 to 1 mm has been cleaned and dried at 110 ^oC for 24 hours, before activation using microwave and 2:1 w/w of Potassium Hydroxide dissolved in 80 ml of distilled water as described previously in the literature.

It is clear in the literature review that there are many factors affecting activation, the ratio of KOH/AC is selected from previous described literature. The factor tested in this study is the activation period. A range of activation periods has been tested to find the optimum activation time that gives the best surface area. The range is 5, 10,15,25,35 minutes and activation methodology as described in section 3.1.4.

3.1.5.3 Ash Content.

As per the procedure described in section 2.6.2.3, three samples from the produced activated carbon has been dried at 110 °C for a few hours until a constant weight is reached. The three samples located in a dried crucible and located in the lab muffle furnace at 650 °C for 1 hour and weighted. The same step is repeated until having no change between the following two weights, following Figure 3-8 show the arrangement of the crucible and furnace.

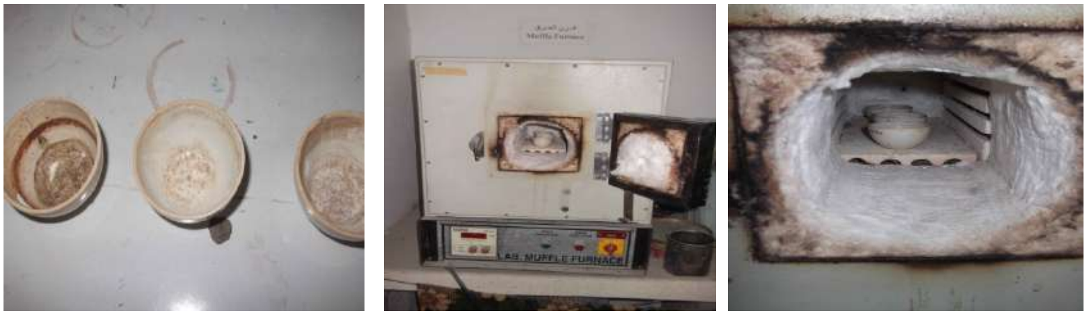


Figure 3-8 Measuring Ash content procedure

3.1.5.4 Bulk Density

Following the same standard procedure described at section 2.6.2.2, three dried samples of 200 ml has been taken on top of a vibrating machine type (DRAGON LAB SK-330-Pro) with a frequency of 250 tap/minutes and the volume is weighted after 5 minutes (1250 tap), repeat the procedure until almost no change in the volume is recorded, then by electronic balance (Satorius BP 221S) the samples are weighted and record it.

3.2 Removal of Detergent by produced Activated Carbon

Detergent is considered as a harmful and toxic compounds, the residual detergents in wastewater is not decomposable and remain in the effluent of treatment plants (El-Said, October 2004). The concentration of detergents in the influent of the treatment plants varies as it depends on the source of detergent such as industrial, domestic and other sources in addition it varies through the daily time depending on the costumes of people and season (summer or winter).

The percentage removal of detergent at the treatment plants depends on the type of these detergents and if it is degradability, in addition to the process used in treatment plants.

Linear alkyl benzene sulphonates (LAS) is the type of detergent used to prepare the synthetic aqueous samples that will be used for all the experiments at the lab.

In this study samples has been taken from Gaza and Rafah wastewater treatment plants on the dates February 2nd, 2013 and analysis of the influent and effluent of wastewater at these plants has been done at Birzeit University testing laboratory in order to find out the limits of the wastewater characteristics. Table 3.2 shows the characteristics of wastewater at Rafah WWTP and Table 3.3 shows Gaza city WWTP characteristics.

Although we are focusing on the detergent concentration in wastewater, the other parameters are measured as per standard methods, it is clear that the average concentration of detergent in wastewater is ranges between 4 and 10 mg/l, but these values can be changed as previously explained (further study to find out the variance of detergent concentration in wastewater by time is needed).

Standard methods for the examination of water and wastewater 19th edition, section 5540C the MBAS (Methylene Blue Active Substances) was used for all the following measurement of the residual detergent in the samples.

Table 3.2: Rafah Wastewater treatment plant – WW analysis

Item	Unit	Wastewater influent	Wastewater Effluent
BOD	mg/l	365	120
COD	mg/l	967	348
TDS	mg/l	2058	2060
TSS	mg/l	480	80
Detergent	mg/l	9	4
TKN	mg/l	82	76
EC	µS/cm	3430	3430
pH		7.92	7.89

Table 3.3: Gaza City Wastewater treatment plant – WW analysis

Item	Unit	Wastewater influent	Wastewater Effluent
BOD	mg/l	365	100
COD	mg/l	945	257
TDS	mg/l	2118	2160

TSS	mg/l	568	50
Detergent	mg/l	8	4
TKN	mg/l	62	45
EC	µS/cm	3530	3600
pH		7.88	7.68

3.2.1 Effect of Adsorption Time

To measure the effect of time on the adsorption of LAS by activated carbon, samples from commercial carbon (Jacobi Carbon – Aqua-Sorb 2000) and samples from produced activated carbon (1 gram each sample) has located in glass bottles. A 50 ml of solution with a concentration of LAS of 10 mg/l has been poured on top of the activated carbon and left for different time ranges (0 , 12, 24, 36, 48, 50, 62, 84) hours at a room temperature of 20-25 °C of an initial pH of the aqueous solution of 6.67.

At the targeted time the samples are filtered and the first 10 ml are excluded, the samples are kept at refrigerator to the last time range to test all of them together, the residual detergent has been measured as per the standard procedure described in section 2.6.1 MBAS (Methylene Blue Active Substances). The spectrophotometer used in measuring the absorbance at 652 nm is UV/VIS spectrophotometer – Chrom-Tech manufacturer Model CT 2200.

Following in Figure 3-9 it shows step by step of measuring the detergent concentration, the tests are done at Bir Zeit University Laboratory for testing material, chemicals used are of high quality and control and experiment has been repeated for three times at same conditions.

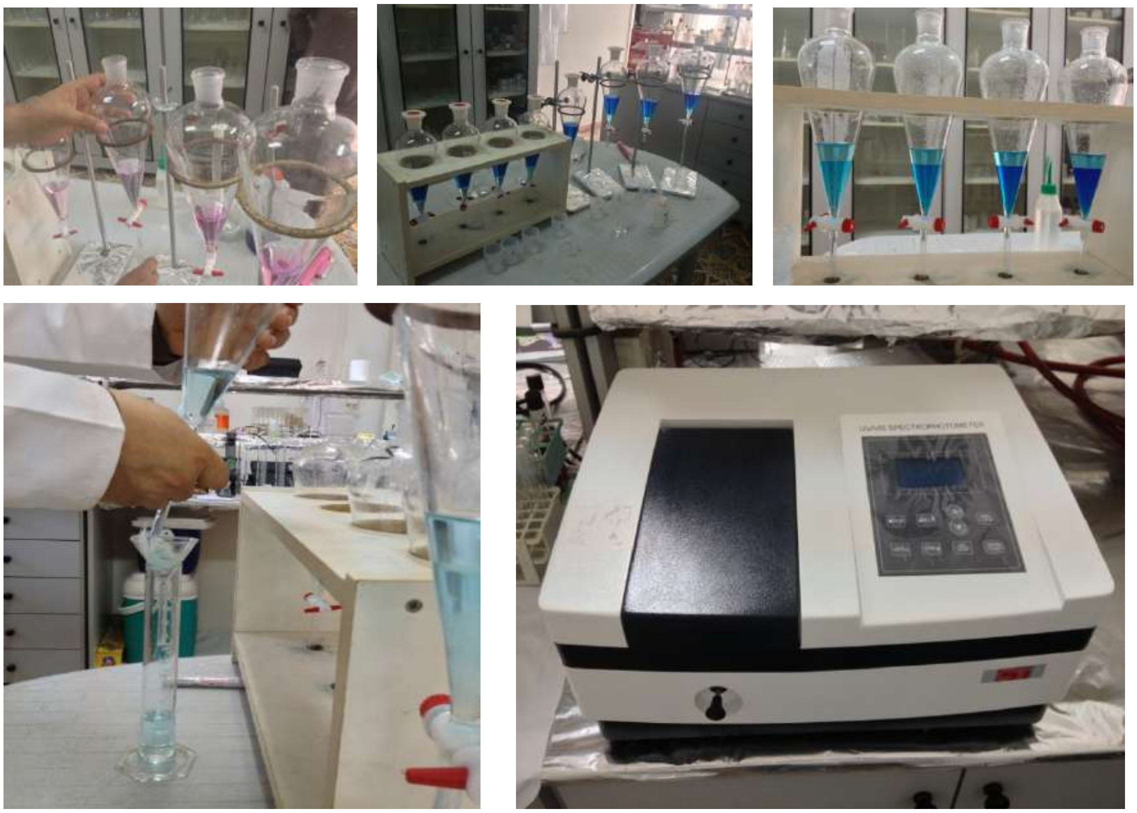


Figure 3-9: Measuring detergent at Laboratory, Step by Step

3.2.2 Effect of Adsorbent Quantity

Samples from produced activated carbon with different weights (1, 2, 3 and 4) grams were used to measure the rate of removal of LAS after 20 hours in a constant room temperature 20 to 25 ^{o}C with initial pH of 6.67. Three samples of 50 ml of solution for each weight with initial concentration of 10 mg/l LAS has been prepared and poured on top of the activated carbon in a glass bottles and left for 20 hours.

The residual LAS has been measured as per MBAS (Methylene Blue Active Substances) procedure described in previous sections and using the same equipments.

3.2.3 Effect of pH

A 50 ml samples with 10 mg/l LAS concentration with an initial pH of 6.67 has been prepared to test the effect of the pH on removal of detergent, pH has been modified to be acidic between a range of 2,98 to 7 and base from 7 to 11.

Few drops (3) of HCL 1 N were added to reach a pH of 2.98, and a few drops (4) of HCL 0.05 N were added to reach pH of 4.65 and one drop of NaOH 0.2 N are added to the sample to reach a pH of 9.65, three drops of 0.2 N of NaOH to reach a 11 pH. The prepared samples of LAS were added each to 1 gram of activated carbon in a glass bottles and left for 20 hours at room temperature of 20-25 ^{o}C. the samples were filtered and the first 10 ml were excluded and the residual LAS has been measured as per standard method described in previous section, also the final pH of each sample has been measured all by Orion pH/ISE meter Model 710 A .

3.2.4 Effect of initial concentration

Three sets of synthetic wastewater contains LAS concentration of (5,10,25,50) mg/l have been prepared with initial pH of 6.67 and poured in a clean glass bottles contains each 1 gram of the produced activated carbon.

The samples have been kept for 20 hours at room temperature of 20 to 25 ^{o}C, then the samples were filtered and the first 10 ml has been excluded and prepared to test the residual LAS as per standard method described in the literature.

The same procedure as previous steps were done but the samples were left till equilibrium (5 days) and the residual LAS in the synthetic samples were measured and recorded.

Additional concentration of 100 and 200 mg/l to equilibrium tests to be used in studying the isotherms.

3.2.5 Isotherms at equilibrium stage

Three sets of synthetic wastewater contain LAS concentration of (5, 10, 15, 20, 25, 50, 100 and 200) mg/l has been prepared with initial pH 6.67. The samples were poured on a clean glass bottles contains each 1 gram of produced activated carbon.

The samples have been kept for 5 days at room temperature 20-25 ^{o}C to allow equilibrium to occur. The samples were filtered and the first 10 ml were excluded and the residual LAS has been measured as per standard method described in previous section. Also pH is measured after five days.

3.2.6 Produced Activated Carbon and Real Wastewater.

A real composite sample from Gaza Wastewater treatment plant was collected from the effluent chamber on Sunday 12th of May 2013, and transported to Bir Zeit University for testing material laboratory.

The sample was filtered, poured in glass flasks and kept in a refrigerator for the following experiments:

3.2.6.1 Detergents, BOD, COD and TKN Removals.

Selected quantities as per standard tests of Detergent, BOD, COD and TKN were taken in the laboratory to measure the concentration of each parameter as the base concentration. Six samples of the filtered wastewater each 50 ml was poured in flasks and 1 gram of the produced activated carbon were added at each flask and left for 20 hours in the room temperature of 20 to 25 ^{o}C and initial pH of 7.68.

The samples were filtered and the first 10 ml was excluded. Detergent concentration, COD and TKN were measured and the samples for the BOD were kept in the incubator to measure BOD after 5 days.

After 5 days the BOD samples were taken out from the incubator and the BOD concentration was measured and recorded.

3.2.6.2 Effect of Initial Concentrations of Detergent on the Percentage Removal

Samples from the effluent and influent of Gaza WWTP has been collected to ensure that different concentrations of detergent are available at the wastewater.

The samples have been filtered and a 50 ml of the filtered wastewater were poured in a glass flasks. A 1 gram activated carbon was added to each of the samples, similar samples without activated carbon were kept at the same conditions (Room temperature 20-25 ^{o}C) to test the initial concentration.

The samples were filtered after 20 hours and the first 10 ml were excluded. Detergent concentration was measured as per standard method presented previously.

CHAPTER 4: RESULTS AND DISCUSSION

Through this chapter the recorded results from the previous experiments will be detailed and discussed.

4.1 Characteristics of char (after Carbonization)

4.1.1 Yield

The collected samples have been taken to measure the **yielding** of the Carbonization process:

- Weight of dried (Dried for 24 hours at temperature 115°C) samples **before** carbonization for three replication is 100 g.
- Weight of the same three samples **after** carbonizations are 23.83, 24.09, 23.77 g,
- Average weight after carbonization = **23.90 ± 0.17** grams and the lost weight is 76.1 g.

Yield after Carbonization = 23.90 ± 0.17 %

Mart´ınez, et al.,(2005); study gave a percentage loss of 74.85%, meaning that the **Yield is 25.15%** when samples carbonized in a muffle furnace heated from room temperature to 600 °C (1 hour) under constant flowing of Nitrogen.

While **Kula, et al., (2007)** when activated by $ZnCl_2$ with different ratios the average yield is 40 to 51%.

It was observed through the carbonization that a very dense smoke is resulted from the burning process in addition to a considerable amount of tar condensed on drops out of the rector, after almost 10 minutes no smoke come out of the reactor which give an indication that the olive seeds are totally carbonized, the process continue another 10 minutes without smoke.

4.2 Characteristics of produced activated Carbon

4.2.1 General Appearance and texture

The following photos at Figure 4-1, Figure 4-2, Figure 4-3 under the microscope shows the surfaces of the char and the activated carbon, it is observed that the surface of the char is quite smooth, dense and planar with occasional cracks or curves this will result a poor or negligible surface area. Figure 4-2, Figure 4-3, show the surface of the produced activated carbon, a clear porous structure is appearing which is responsible for the produced surface area.

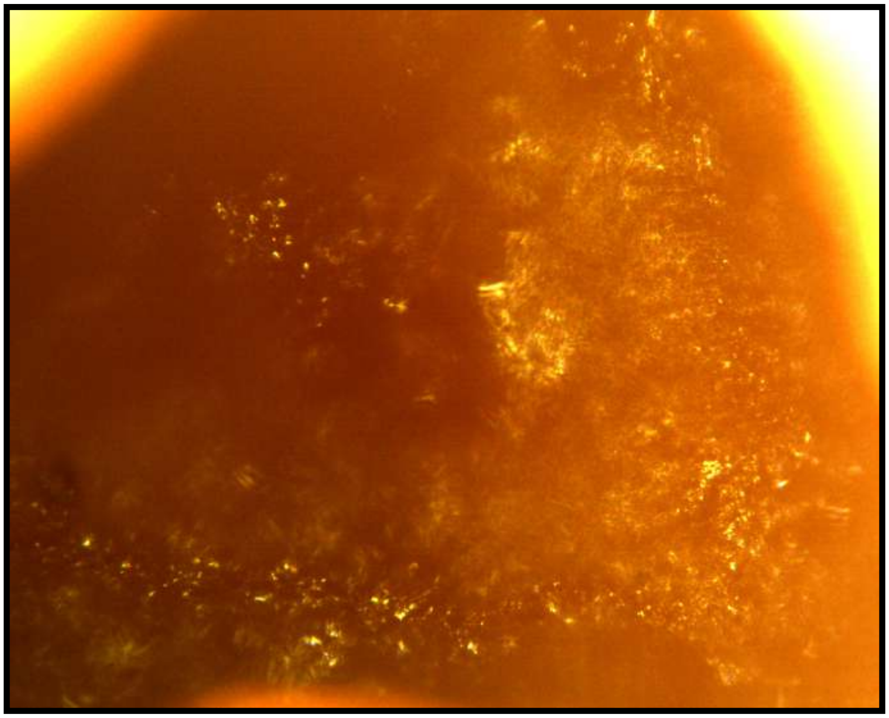


Figure 4-1 Char under Microscope 200X

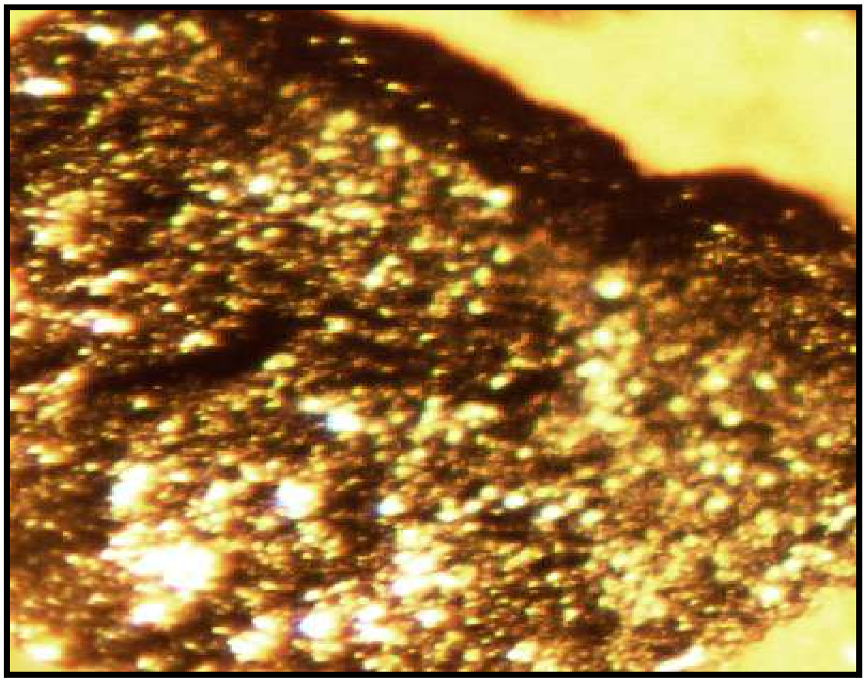


Figure 4-2 Activated Carbon under Microscope 200X

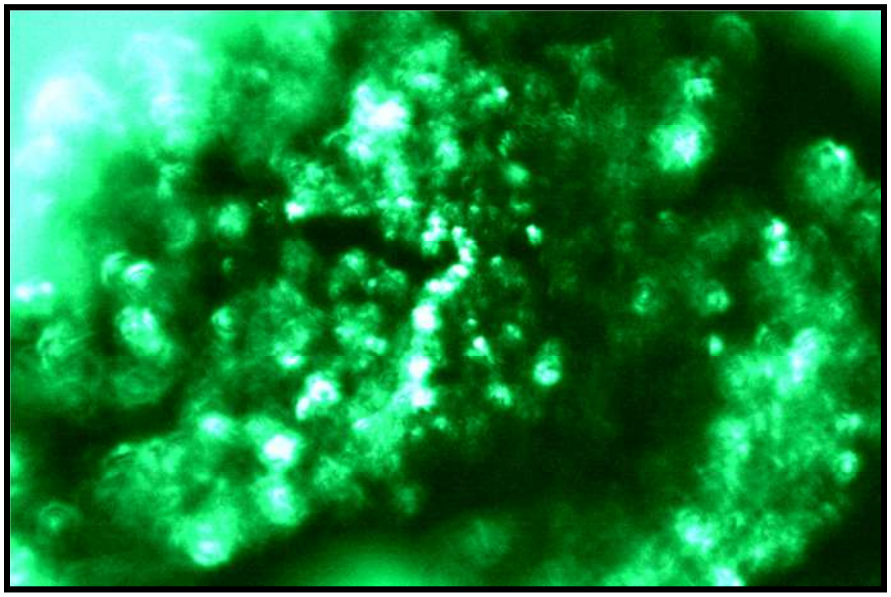


Figure 4-3 Activated Carbon under Microscope 400X

4.2.2 Surface Area

4.2.2.1 Commercial Activated Carbon

The resulted isotherm graph for the acetic acid and produced activated carbon is as shown in Figure 4-4

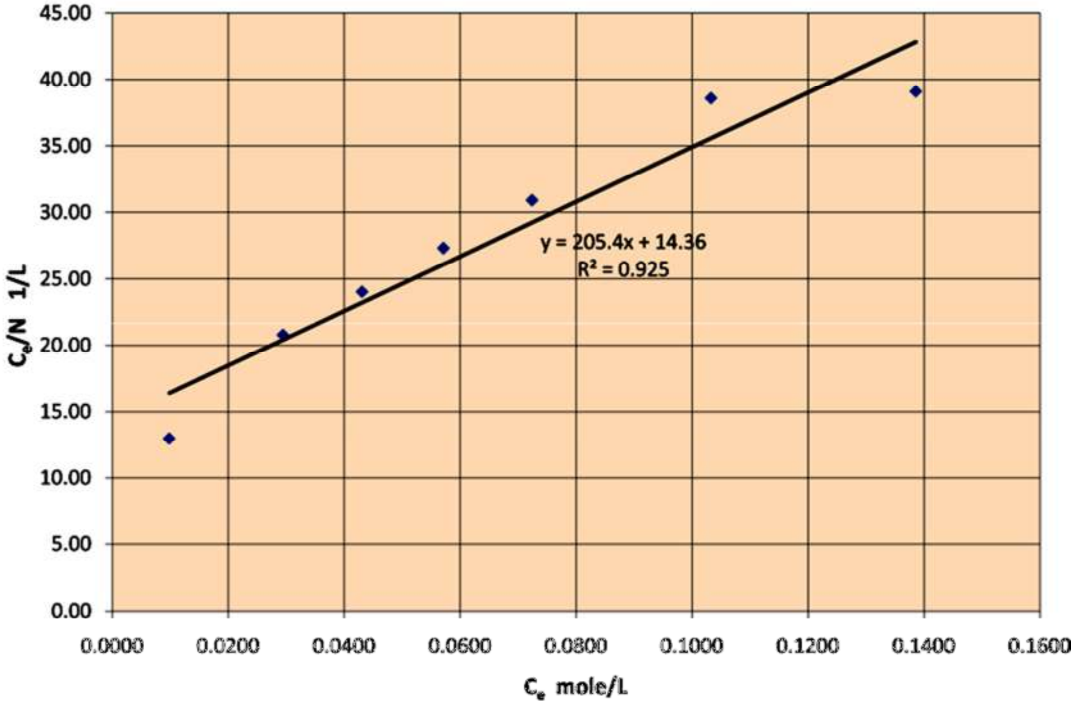


Figure 4-4 Acetic Acid, Commercial activated carbon Isotherm

The measured /calculated surface area by acetic acid Isotherm (Calculation at Appendix A) is 615 m^2/g, while the surface area measured by the manufacturer by BET N_2 is 1100 m^2/g therefore a factor of **1.7** was considered to find out the BET N_2 of the produced activated carbon from the olives seeds as shown later.

“The surface areas of commercial AC samples, (with known surface areas >1000m^2/ g) were studied using the acetic adsorption method, and the measured value was 850m^2 /g” (El-Hamouz, et al., 2006).

4.2.2.2 Produced Activated carbon

The resulted isotherms for acetic acid and the produced activated carbon at different avtivation periods are as appears in the following graphs, further calculations are included in Appendix A,

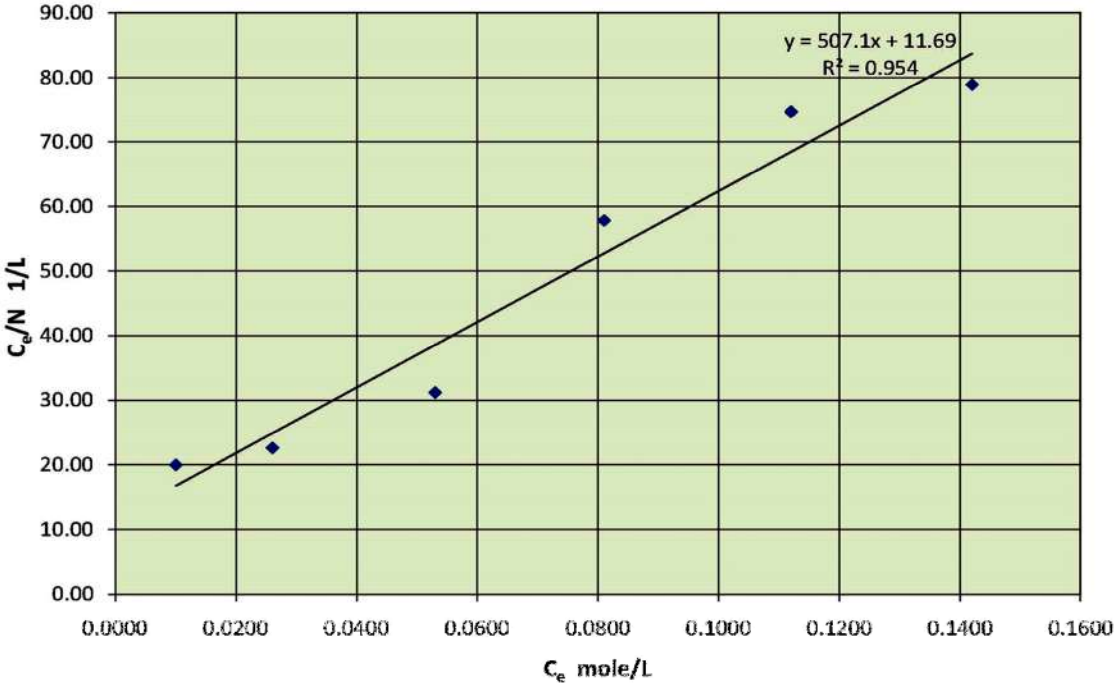


Figure 4-5 Acetic Acid, Produced activated carbon Isotherm, 5 min. Activation

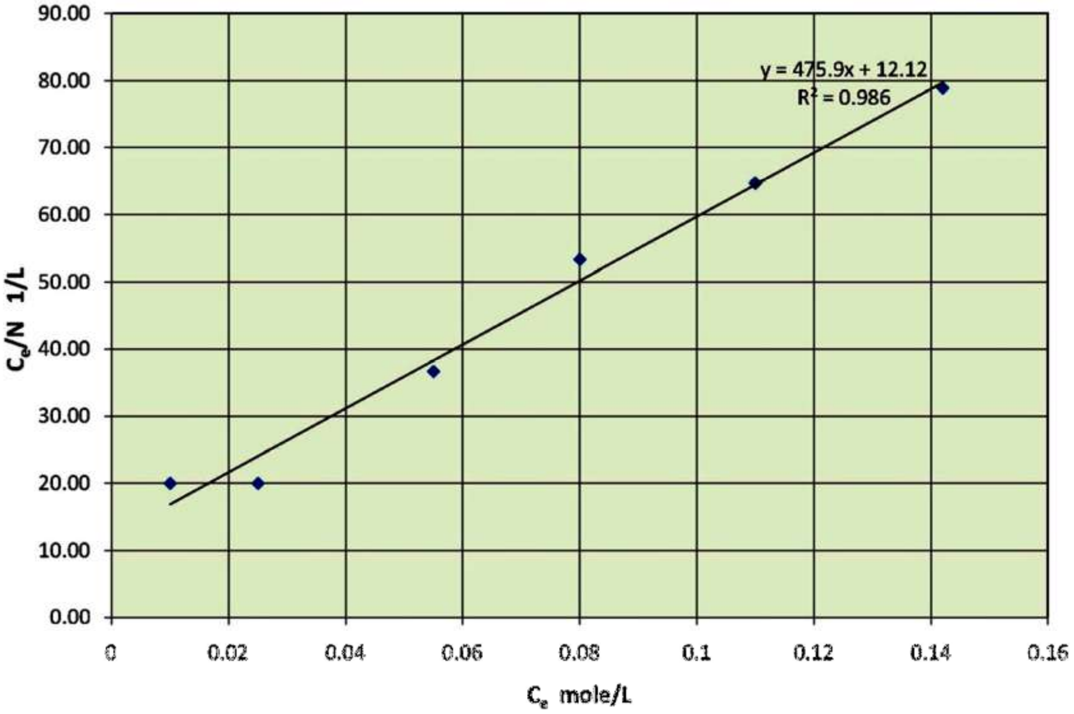


Figure 4-6 Acetic Acid, Produced activated carbon Isotherm, 10 min. Activation

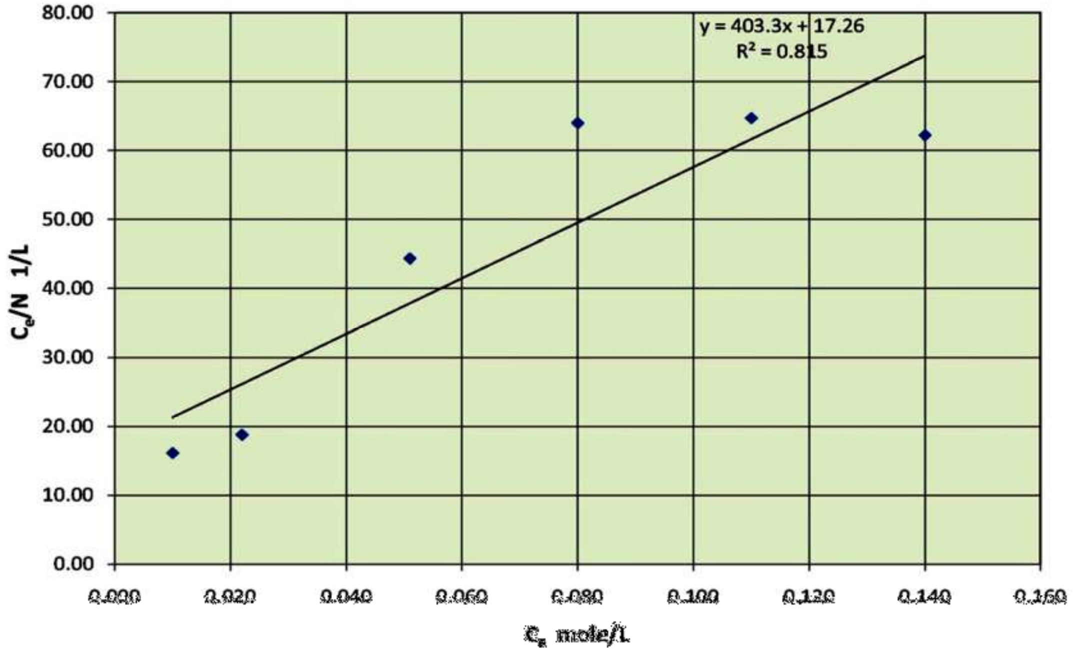


Figure 4-7 Acetic Acid, Produced activated carbon Isotherm, 15 min. Activation

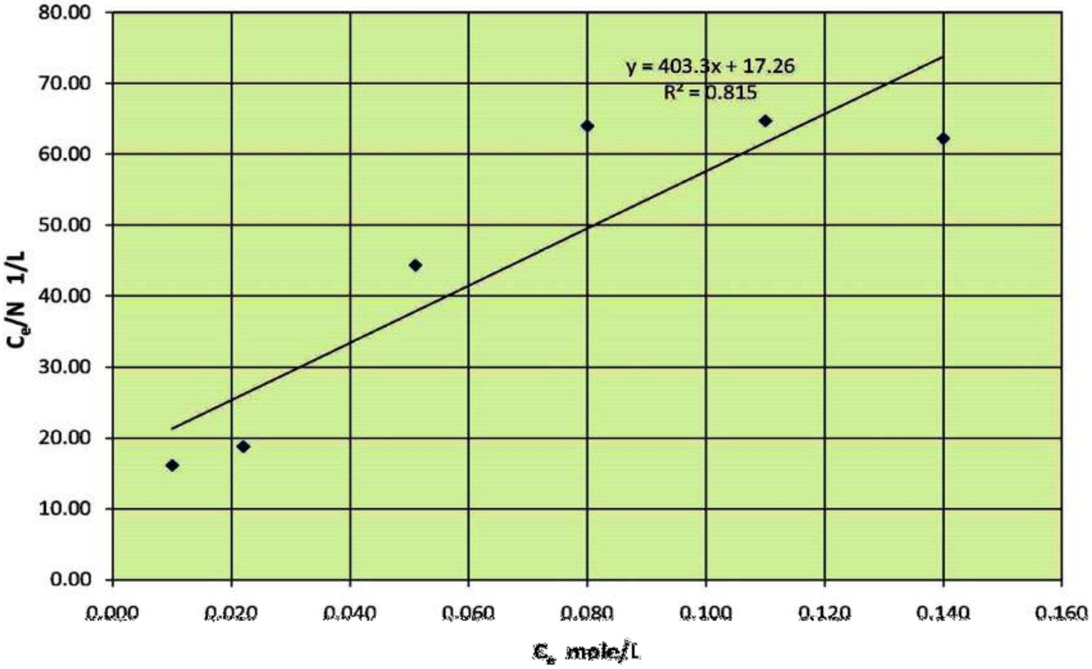


Figure 4-8 Acetic Acid, Produced activated carbon Isotherm, 25 min. Activation

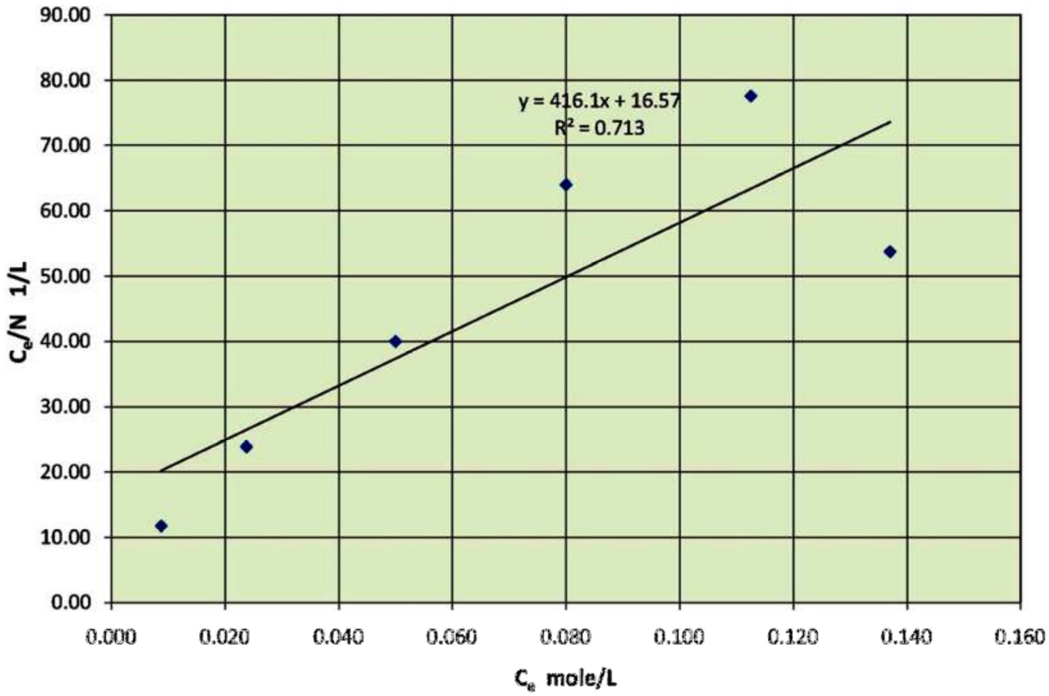


Figure 4-9 Acetic Acid, Produced activated carbon Isotherm, 35 min. Activation

The resulted surface area at different activation period calculated in appendix A and summarized in the following Table 4.1:

Table 4.1: Resulted surface area with various activation period

Time of Activation	Surface area Acetic Acid	Equivalent Surface Area BET N_2
Min	m^2/g	m^2/g
5	249	423.89
10	266	452.45
15	321	545.47
25	314	533.29
35	304	516.62

It is observed that by increasing the activation period the resulted surface area increased in the range of 5 to 20 minutes and started to decrease in the range above 20 minutes. Figure 4-10 describes clearly the change of the surface area by increasing the activation period.

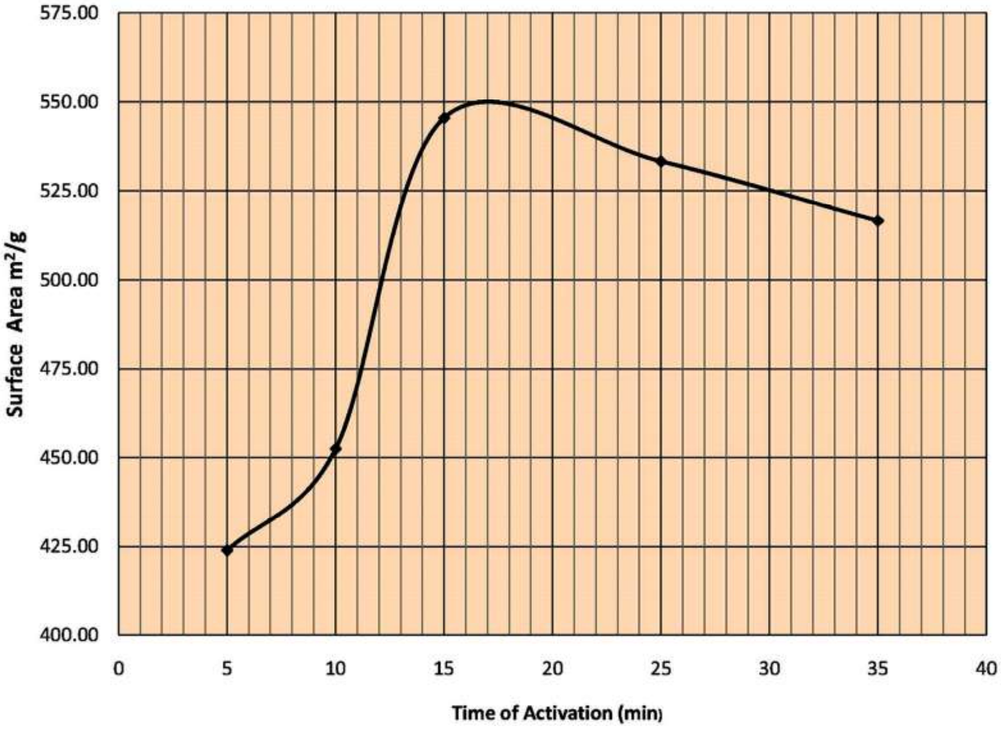


Figure 4-10 Activation period vs. surface Area

It is observed that, the change in the surface area, resulted from lower activation period (5 minutes) and optimum (17 minutes) is 125 m^2/g (30%), while the change between the optimum and the highest activation period (35 minutes) is 34 m^2/g (6%) which can be considered not significant. A 20 minutes activation is considered as the optimum activation period (additional 3 minutes from optimum to allow for variance in opening and closing elapsed time). The remaining quantity of char has been activated based on this period. The phenomenon implied that the formation of new pores became less significant with the activation proceeding, and the micro-pores or meso-pores were continuously widened into larger ones. Furthermore, they might also be destroyed after long time exposure to the microwave radiation. Similar observation was recognized when activated carbon was produced from cotton stalk by microwave activation with the assist of KOH (Deng, et al., 2010).

All the char has been activated at 20 minutes under the same conditions described in the literature and a random sample has been tested and the result as shown in calculations in Table A.7 - Appendix A and in Figure 4-11. **The average BET N_2 surface area resulted is 546 m^2/g with $R^2 = 0.969$**

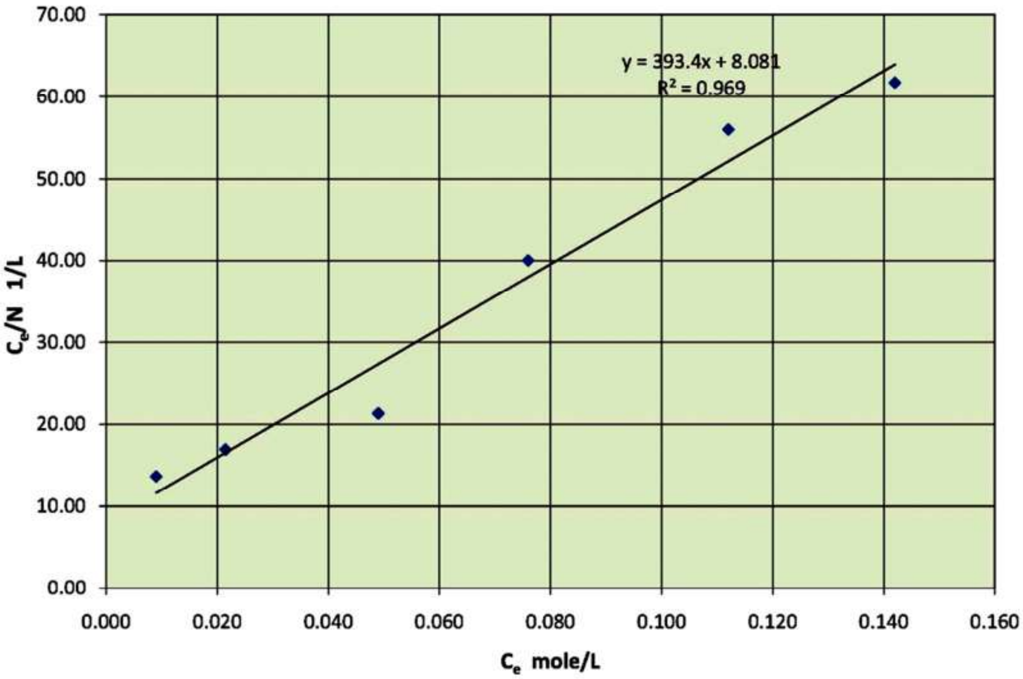


Figure 4-11 Sample from the whole activated char at 20 minutes

4.2.3 Ash content

The following Table 4.2, shows the resulted average **Ash content of the produced activated carbon is 1.08 ±0.38 %.**

Table 4.2: Ash content calculation

Sample NO.	Sample Wt.	Wt. of Ash	Ash Content
	gram	gram	%
1	**1.32**	0.02	1.52
2	**1.21**	0.01	0.83
3	**1.10**	0.01	0.91
Average Ash content			**1.08 ± 0.38**

It is observed that the ash content is low compared to other studies such as (El-Hamouz, et al., 2006) where the ash content is less than 6%, this could be referred to the low content of residual minerals in the seeds is typically 2.99 g/kg (El-Sheikh, et al., 2003), in addition to multiple cleaning of the seeds at the preliminary stages of samples collection and preparations.

4.2.4 Bulk Density

The results of measuring the bulk density for the three samples was the resulted values are 88.5, 89.4, 88.9 grams.

Table 4.3: Bulk density calculation

Sample No.	Sample Weight (g)	Volume ml	Density Kg/m^3
1	88.5	200	442.5
2	89.4	200	447
3	88.9	200	444.5
Average Bulk Density			**444.67 ± 2 kg/m^3**

4.2.5 Total Yield

As calculated in section 4.1.1 measured **Yield after Carbonization = 23.90 %** , three samples of 30 grams of char has been considered in measuring the yield by activation with microwave for 20 minutes and assessed by KOH 1:2 w/w.

The three samples has been cleaned and washed with distilled and dried in the oven for 24 hours at 110 ^oC to ensure no moisture in the samples and reach constant weight, the weights where as following (25.3, 24.9 25.2 grams).

Average weight is 25.1± 0.2 grams and the **yield in activation is 83.77%**

Total yield is (0.8377 X 23.90 %) is 20.02%

Mart´ınez, et al., 2005; when activated the olives seeds has a tota yield varies between 13.02 to 20.21% based on the ratio of KOH to AC w/w.

Summary of the produced activated carbon characteristics and comparison with other produced activated carbon from Olives and other materials are shown in Table 4.4.

Table 4.4: Produced Activated carbon compared to others

Activated Carbon	Particle size mm	Surface Area m^2/g	Ash Content %	Bulk Density Kg/m^3	Reference
Produced activated Carbon (Olive Stone)	0.6 - 1	546	1.08	444.6	This Work
Olive Waste	0.045 – 0.2	400 – 1200*	< 6	480	El-Hamouz, et al., 2006
Olive Stone	0.1 – 0.3	960	**-**	-	Mart´ınez, et al., 2005
Olive Stone	1	65 – 300*	**-**	-	El-Sheikh, et al., 2003
Olive mill waste	1 – 1.4	345 – 1768*	7.3 -29*	450 – 680*	Moreno-Castilla, et al., 2000
Commercial AC					
Jacobi Carbon – Aqua-Sorb 2000	1.5 - 2	1100	-	470	Jacobi Carbon
WF - GAC - Coconut-Gold	-	1000 -1100	3	500 - 540	Winfield Industry, Inc

∗: the variance depends on different procedure of Carbonization and Activation

The equivalent BET N_2 surface area of the produced activated carbon is relatively high compared to the produced ones in previous studies. A direct measurement by N_2 adsorption is required may be one time to check the correction factor used in the study. The Ash content of the produced activated carbon is the lowest and this is improvement to the work, while the bulk density is within the average value of other studies.

4.3 Detergent Removal

The produced Activated carbon was tested as adsorbent in the removing of detergents from a synthetic solution in the following sections. As referenced previously in chapter 2, there are many factors affecting the adsorption process, which used in this study. Following are the results of the effects of these factors on the adsorption process:

4.3.1 Effect of adsorption time on removing of detergent from synthetic solution

Following is the result of effect of the adsorption time on the detergent removal:

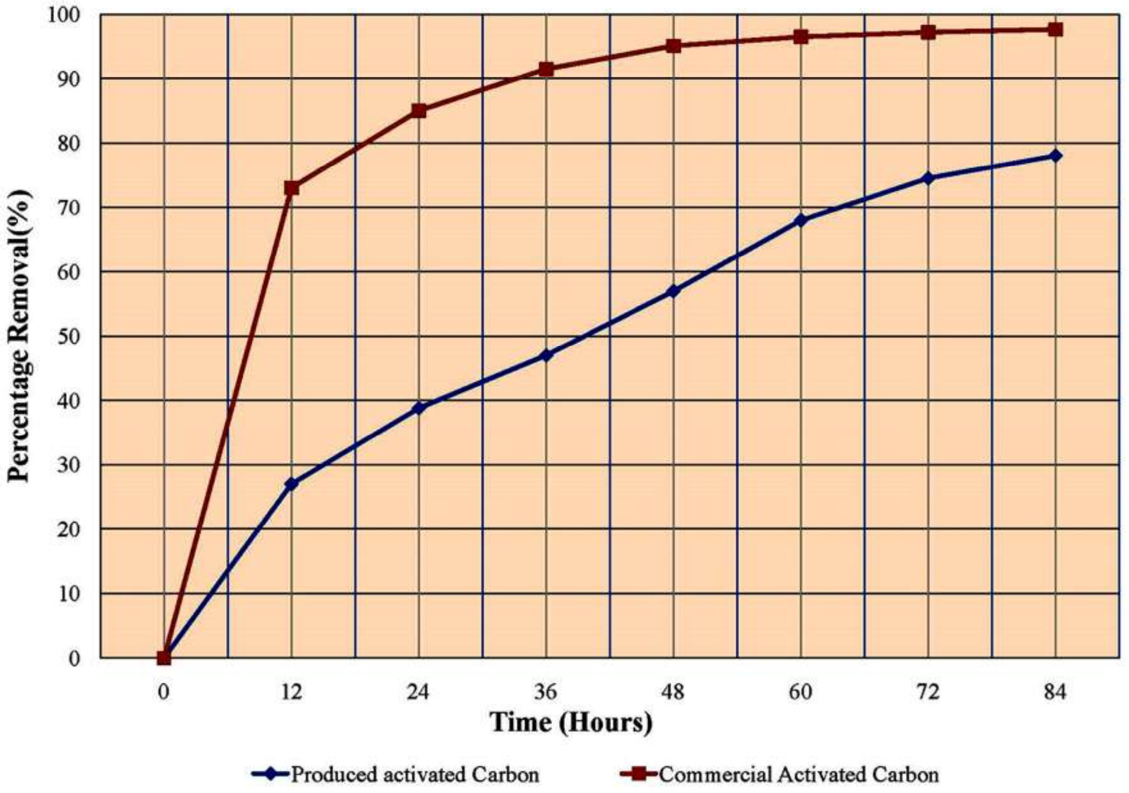


Figure 4-12 Effect of adsorption time on detergent removal

It is observed that the rate of removal of LAS by the commercial carbon is very high compared to the produced activated carbon, (3 times) in the first 12 hours. It is also observed that the rate of removal for the produced activated carbon in the first 24 hours (39%) is high compared to the following repeated 24 hours (18%, 17%) and 3.5% in the following 12 hours. It can be considered that the optimum time for maximum rate of removal is the value between 12 and 24 hours, 20 hours is taken for other experiments as optimum time for adsorption .

The phenomena of decreasing the sorption rate by time can be related to the high surface film of the activated carbon compared to produced micro-pores and meso-pores which will affect the rate of adsorption on a later stage of the adsorption process, the three stages of adsorption is described by Weber (1974). He stated that "There are three primary rate steps in the adsorption of materials from solution by granular activated carbon. First is the transport of the adsorbate through a surface film to the exterior of the adsorbent ('film diffusion'); second is the diffusion of the adsorbate within the pores of the adsorbent ('pore diffusion'); third is adsorption of the solute on the interior surfaces bounding pore and capillary spaces. For most operating conditions transport of adsorbate through the 'surface film' or boundary layer is rate-limiting”.

4.3.2 Effect of Adsorbent Quantity

The effect of adsorbent quantities in removing of LAS from the solution is as shown in the following graphs.

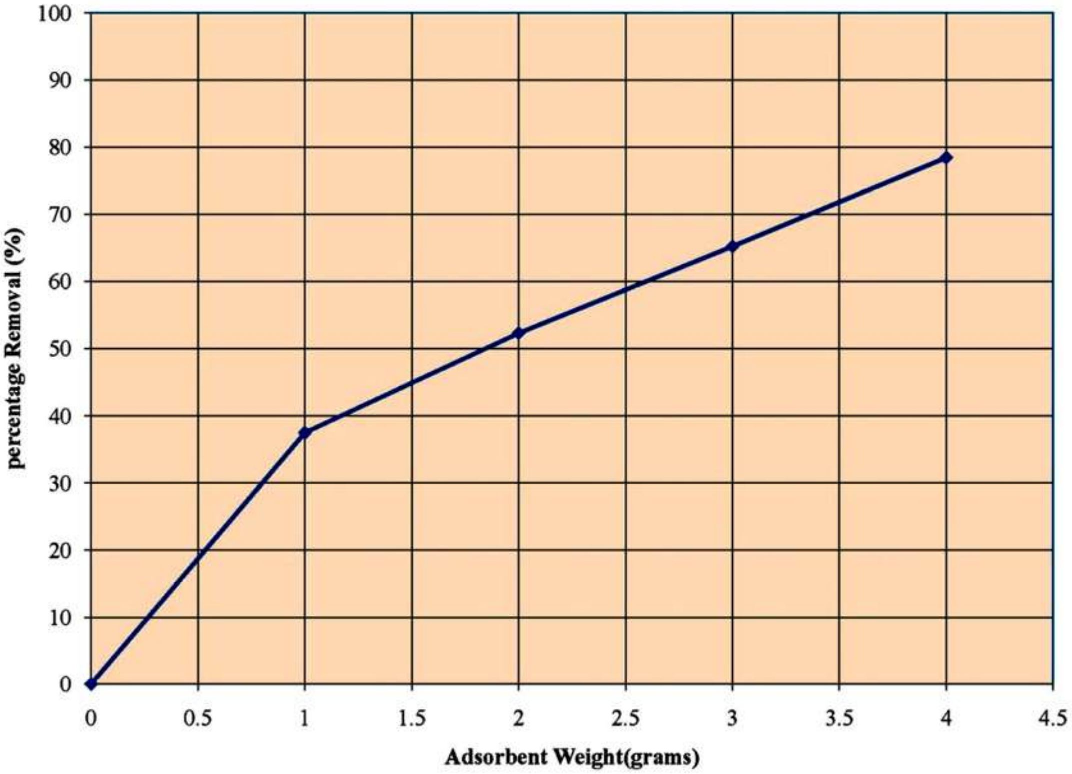


Figure 4-13 Effect of adsorbent Quantity on detergent removal

From Figure 4-13 the rates of removal for each quantity has been calculated and Figure 4-14 show it,

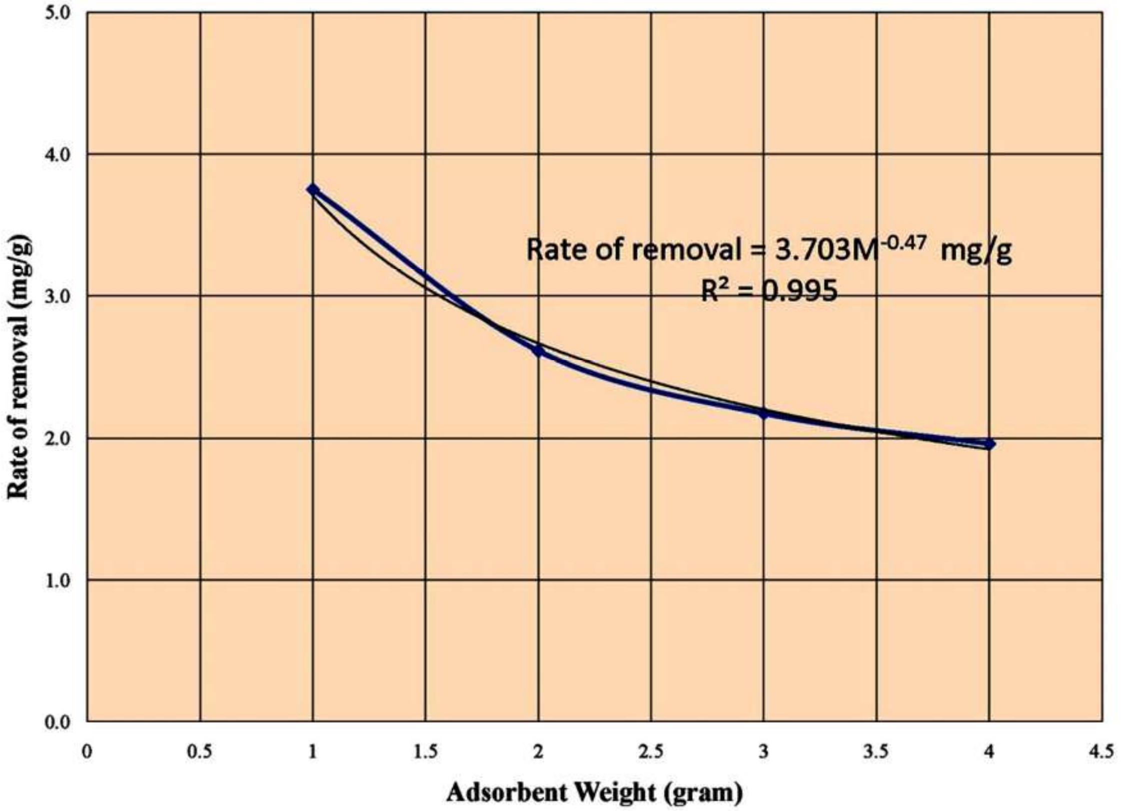


Figure 4-14 Rate of Removal vs Adsorbent Quantity

Although the percentage of adsorption increases by the increase of the adsorbent quantity, the amount adsorbed by unit mass decreases. As with 1 gram of the activated carbon about 37% of the 10 mg/l of LAS is removed at 20 hours, while the 2 grams at the same time did not remove double of the rate (74%), only 52% has been removed, with a removal rate of 26% per a gram. The following weights (3 and 4 grams) have a rate of removal about 20 % per gram.

This phenomena can be referred to the un-saturation of the adsorption site through the adsorption process described by Ozacar 2005, (Malik, et al., 2006)

The rate of removal is not following a linear relation with the adsorbent quantity it is close to be a power relation (Rate of removal = 37.03 $M^{-0.47}$) per each gram of the adsorbent with a regression of R^2=0.995 (M is Carbon Mass).

4.3.3 Effect of pH

The experiment has been repeated for three times to measure the effect of different levels of pH on removal of LAS by the produced activated carbon and the following results have been achieved (Figure 4-15).

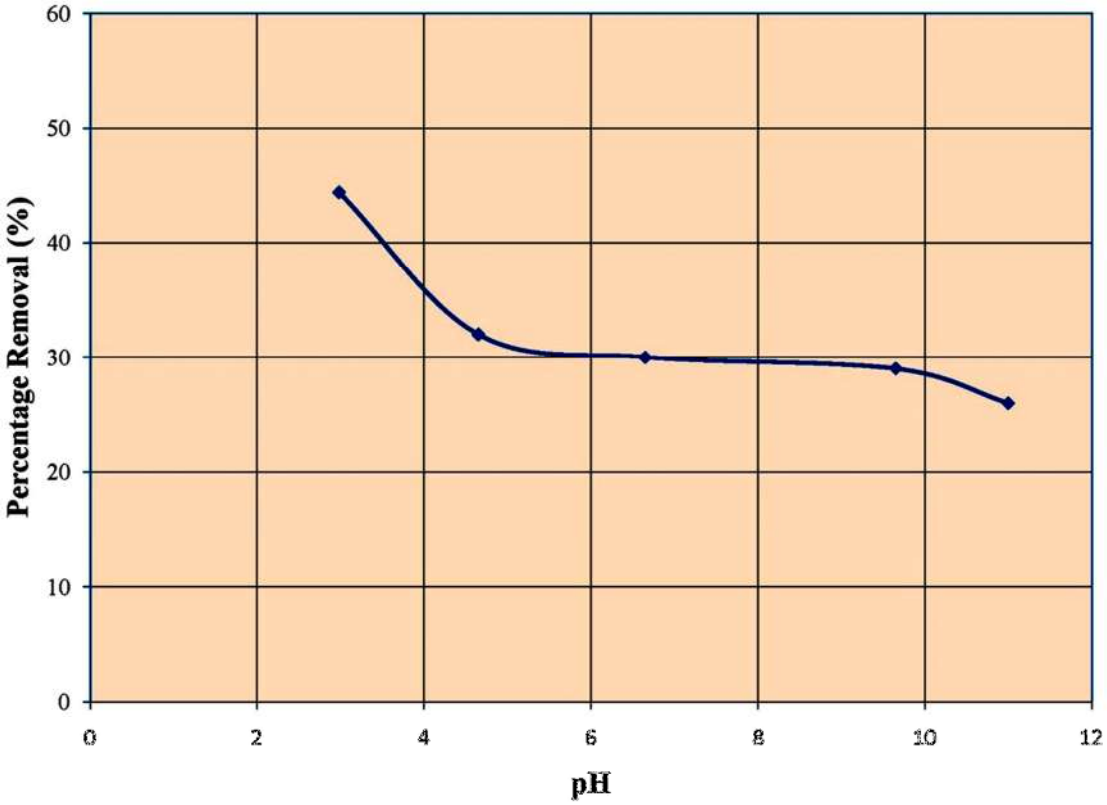


Figure 4-15 Effect of pH on Removal of LAS

It is observed that the percentage of removal of LAS at a pH ranges between 3 to 5 decreases while between the range of 5 to 9 no significant changes in the percentage removal, from 9 to 11 the removal rate decreases again. It is worth to note that the pH of activated carbon when located in a distilled water of 7.26 pH and left 20 hours the final pH reaches 7.40 at the same conditions of the experiment.

The final pH of the samples has been measured before testing the rate of removal, the resulted shown in Figure 4-16, where the produced activated carbon works as a buffer, by increasing the pH of the solution at acidic zone to be neutral and reduce the base pH from10 pH to neutral. Although the pH of the activated carbon in a base it did not increase the pH at the base side.

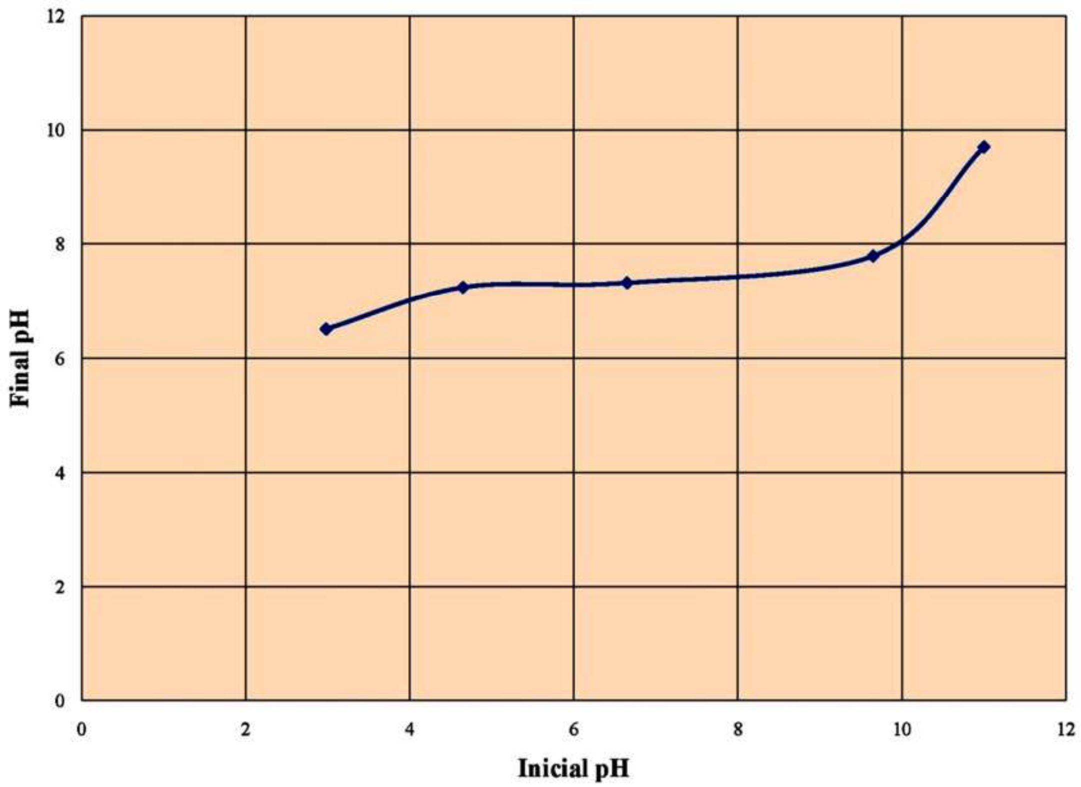


Figure 4-16 Change in Initial pH by change of Activated Carbon Quantity

The decrease of adsorption at low and high pH can be referred to the increase of the hydrogen and hydroxide ions, which are adsorbed quit strongly compared to other ions available in the solute like LAS ions, in addition water solubility is expected to increase with increasing polarity, this will result adsorption decreases as polarity increases (Weber, 1974).

The effect of pH in removing detergent can be considered negligible at a range of 4.5 to 8.5 where most of wastewater pH falls in this range.

4.3.4 Effect of Initial concentration and Isotherms

The effect of the initial concentration on the removal of LAS after 20 hours and five days (equilibrium period) is shown in the following Figure 4-17. At equilibrium (5 days), 98% of LAS was removed by 1 gram from the produced activated carbon for the range of concentration 5 to 25 mg/l and it is clear that the difference is not significant. After 20 hours, the percentage removal drops from 42% to 34% when the initial concentration varies between 5 to 25 mg/l .

It is also observed that for the range of concentration greater than 25 mg/l at both equilibrium time and after 20 hours, the percentage removal is dropped from 98% to 75% and 34% to 6%. At greater concentration (larger than 50 mg/l), the percentage removal continue dropping to reach 65% at initial concentration of 200 mg/l.

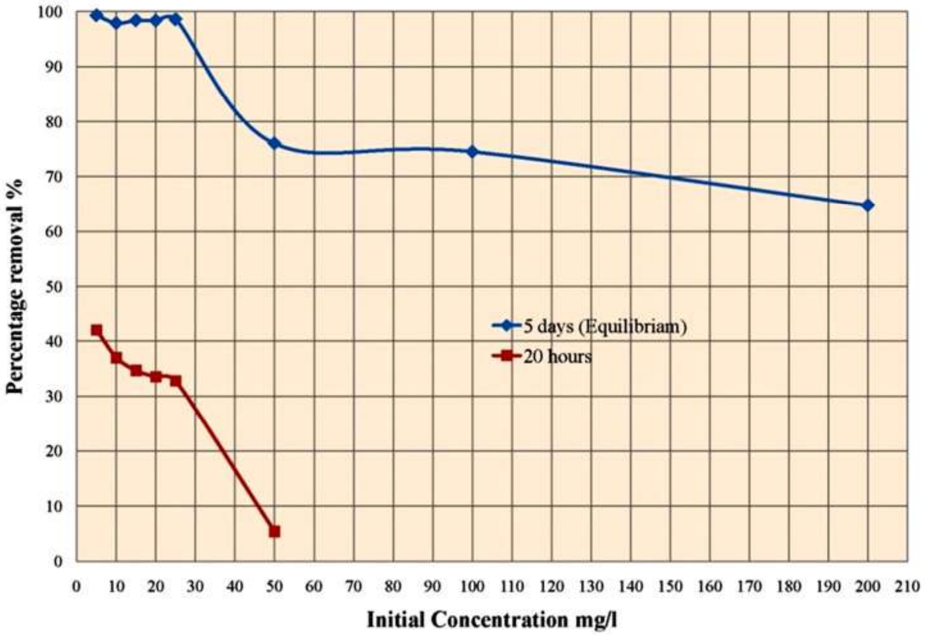


Figure 4-17 Effect of Initial Concentration on the Percentage Removal

The above phenomena can be attributed to, at lower concentration the ratio of the initial number of LAS molecules to the available surface area of the activated carbon is low. However, at high concentration the available sites of adsorption becomes fewer, and hence the percentage removal of LAS is dependent upon the initial concentration

It can be concluded from Figure 4-17 that the produced activated carbon has a high capacity in removing LAS but in a slow rate, also when LAS concentration is greater than 25mg/l the initial concentration has a serious effect on the removal percentage.

In order to study the behavior of the activated carbon in removing LAS with different initial concentration at equilibrium stage, the Isotherms were studied at the three different ranges (5 to 25) mg/l, (25 to 50) mg/l and (50 to 200) mg/l of LAS concentrations . Figure 4-18 show Freundlich isotherm for LAS adsorption by produced Activated Carbon with initial pH of 6.67 and at temperature of 20-25 ^{o}C, for the range of concentration 5 to 25 mg/l.

Figure 4-19 show Langmuir isotherm for LAS adsorption onto produced Activated Carbon (C_o from 25 to 50 mg/l), while Figure 4-20 show Langmuir isotherm for LAS adsorption onto produced Activated Carbon (C_o from 50 to 200 mg/l) at the same condition of temperature and initial pH.

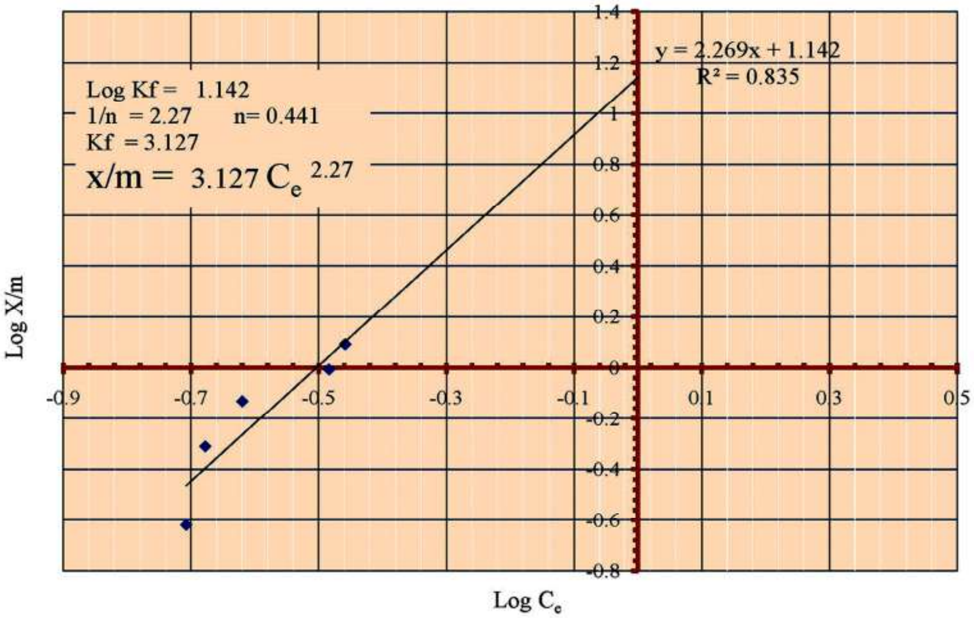


Figure 4-18 Freundlich isotherm for LAS adsorption onto produced Activated Carbon (C_o from 5 to 25 mg/l)

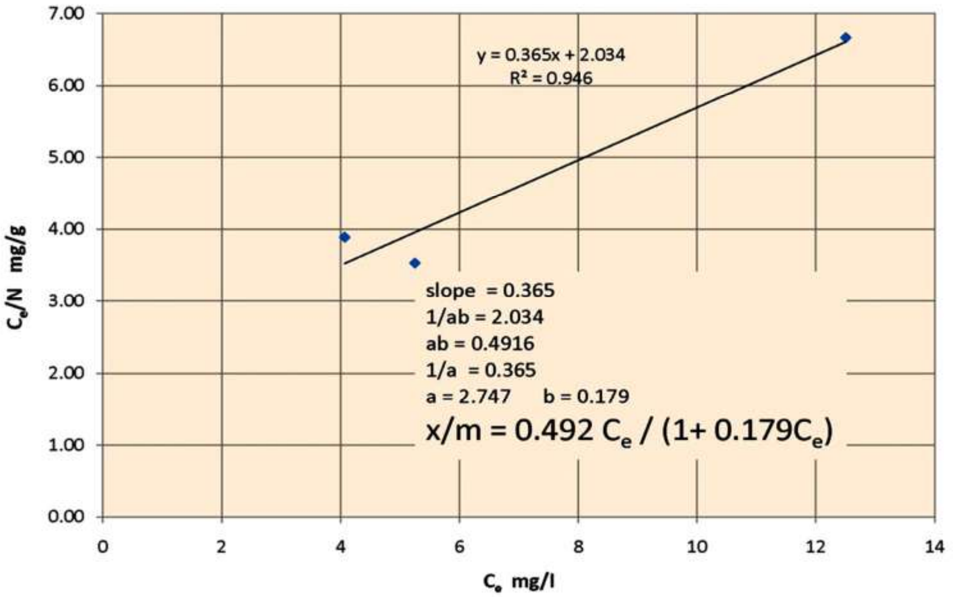


Figure 4-19 Langmuir isotherm for LAS adsorption onto produced Activated Carbon (C_o from 25 to 50 mg/l)

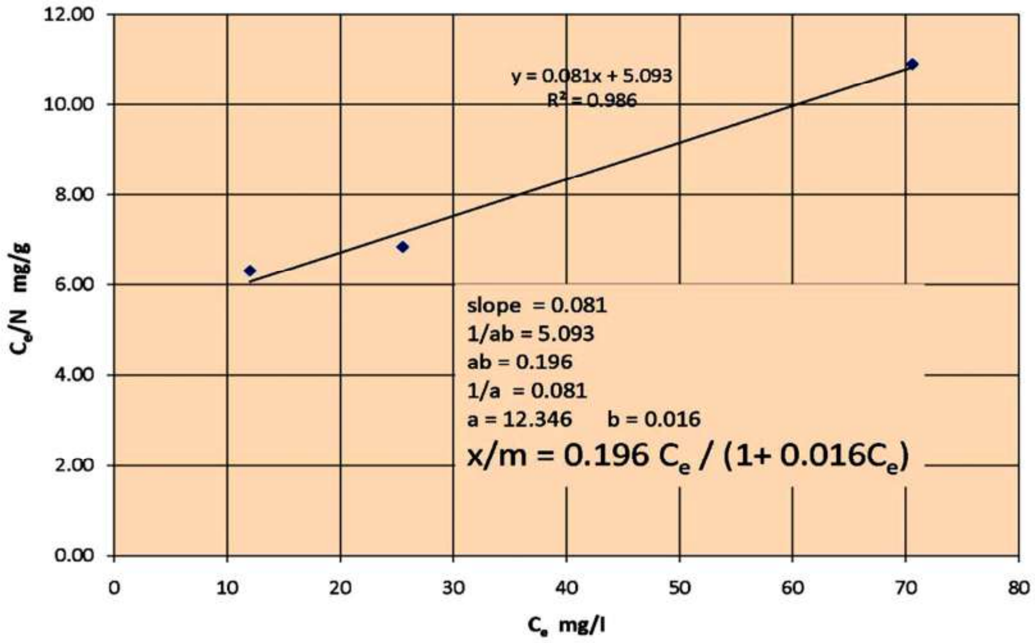


Figure 4-20 Langmuir isotherm for LAS adsorption onto produced Activated Carbon (C_o from 50 to 200 mg/l)

Where :

X mass of LAS adsorbed and equal to ($C_o - C_e$) x V where

C_o : the initial concentration mg/l,

C_e : the equilibrium concentration mg/l,

V : the volume of the sample (50 ml) in the experiments in liters,

M is the mass of the adsorbent (Activated Carbon) gram

N is X / M (Langmuir)

The resulted **<u>Freundlich Isotherm Equation</u>** for the range of concentrations 5 to 25 mg/l can be derived as following:

$$((C_o - C_e) * V / M) = 3.127\, C_e^{2.27}$$

Freundlich factors are K_f and n are found as (3.127 and 0.441).

The resulted **Langmuir Isotherm Equations** for the range of concentration 25 to 50 and 50 to 200 mg/l can be derived as following respectively:

$$((C_o - C_e) * V / M) = 0.492\, C_e / (1+0.179\, C_e)$$

$$((C_o - C_e) * V / M) = 0.196\, C_e / (1+0.016\, C_e)$$

Langmuir factors a and b are found as (12.346 l/mg and 0.016)

Where the capacity of the produced activated carbon can be presented for adsorbing LAS from a synthetic solution, and can be used in providing description of the functional dependence of capacity on the concentration of LAS and the mass of the activated carbon.

The isotherm shapes may tell if adsorption is ''favorable'' or ''unfavorable'' using the Langmuir-type adsorption process. The isotherm shape is classified by a dimensionless constant separation factor, r, where $r = 1/(1 + aC_o)$. Smaller values, $r < 1$, represent favorable adsorption, whereas larger values represent unfavorable adsorption. In all LAS concentration, (r) is very much lower than 1 (0.016 to 0.0004), which give a result that LAS is a favorable in adsorption by activated carbon.

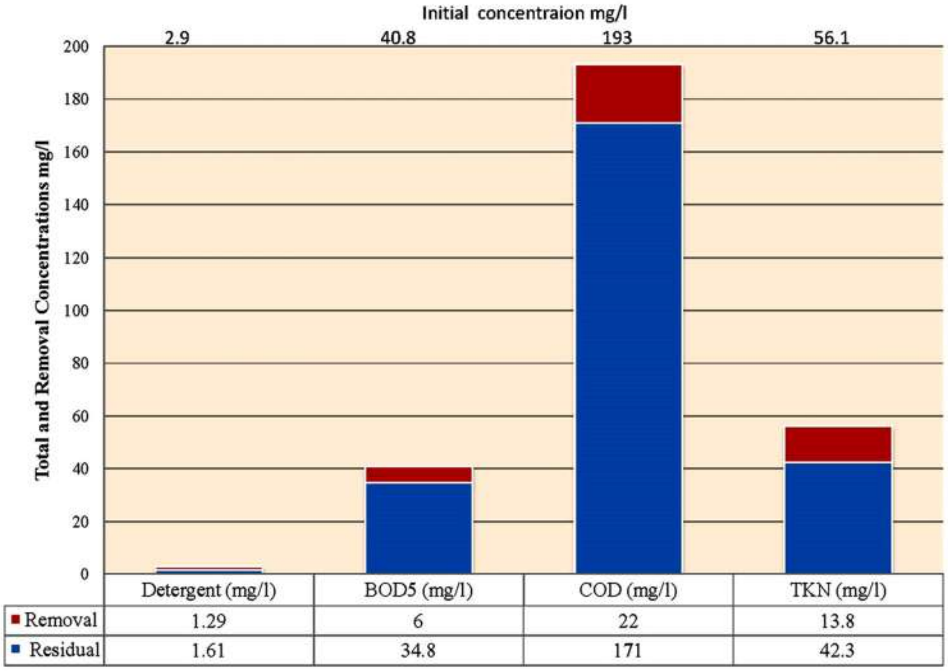
4.4 Real Wastewater Samples and Detergent Removal

Analysis of samples collected from wastewater treatment plants shown in Table 3.2and Table 3.3, where, the results show that through the biological treatment process in wastewater treatment plant there is a percentage removal ranges between 50 to 55%. Most of this amount of mass either removed by adsorption to sludge or organic base detergent degraded through the treatment process. The residual remains at the effluent of the treatment plants ranges between 5 to 10 mg/l depending on the treatment process.

Through the previous experiments the synthetic solution with LAS has been used to find out the properties of the produced activated carbon and check the possibility of removing detergent in general from aqueous solution.

The following experiments have been done on a real wastewater collected from Gaza wastewater treatment plant.

Figure 4-21 show the initial concentration of detergent, BOD, COD, and TKN, the removed and the residual concentration after 20 hours of adsorption by1 gram of the produced activated carbon.



	Detergent (mg/l)	BOD5 (mg/l)	COD (mg/l)	TKN (mg/l)
🟥 Removal	1.29	6	22	13.8
🟦 Residual	1.61	34.8	171	42.3

Figure 4-21 Removal of detergent, BOD, COD and TKN from Real Wastewater Samples by Activated Carbon

Figure 4-22 show the calculated percentage removal of the parameters, where the highest percentage recorded for the removal of the detergent as 44.5% and other parameters BOD, COD and TKN are 14.7%, 11.4% and 24.6 %, respectively.

It is also noticed that there is a competition between the parameters through the adsorption process, which can be clear when calculating the mass removed (Detergent;0.065 mg, BOD;0.30 mg, COD;1.1 mg and TKN 0.69 mg) which ranges from 5 to 17 times of the amount removed from the detergent.

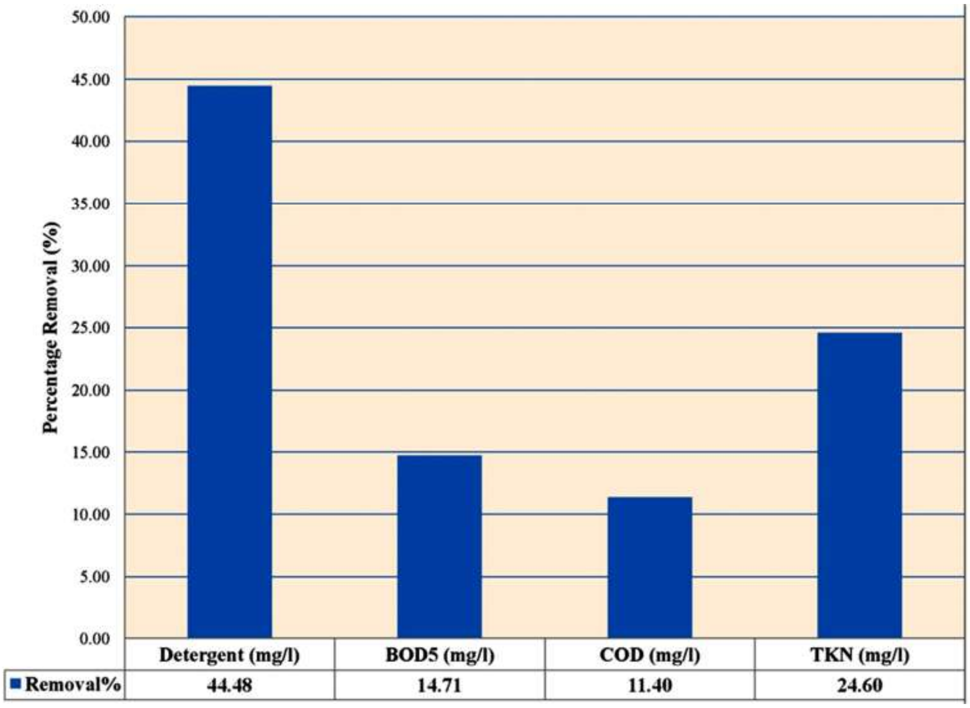


Figure 4-22 Percentage Removal of Real Wastewater Parameters by Activated Carbon.

The effect of competition can be understood because organic components at wastewater may mutually enhance adsorption, may act relatively independently, or may interfere with one another (Weber, 1974). The adsorption of one substance will tend to reduce the number of open sites at the carbon surface and, hence, the removal of the adsorbent either be controlled by the other substance positively or negatively based on many other factors need further study to understand it properly.

4.4.1 Effect of Initial Concentration of Real wastewater

The result of the initial concentration of the real wastewater is shown in the Figure 4-23. The percentage removal after 20 hours of adsorption dropped from 44.5% to 34.9% as the initial concentration rises from 2.9 mg/l to 11.4 mg/l respectively, however the mass adsorbed increased from 0.065 mg to 0.20 mg (three times) by one gram of activated carbon.

Comparing the behavior of the adsorption process for synthetic samples and real wastewater, concerning the percentage of removal, it is clear that there is no significant difference within the range of concentration of 15 mg/l.

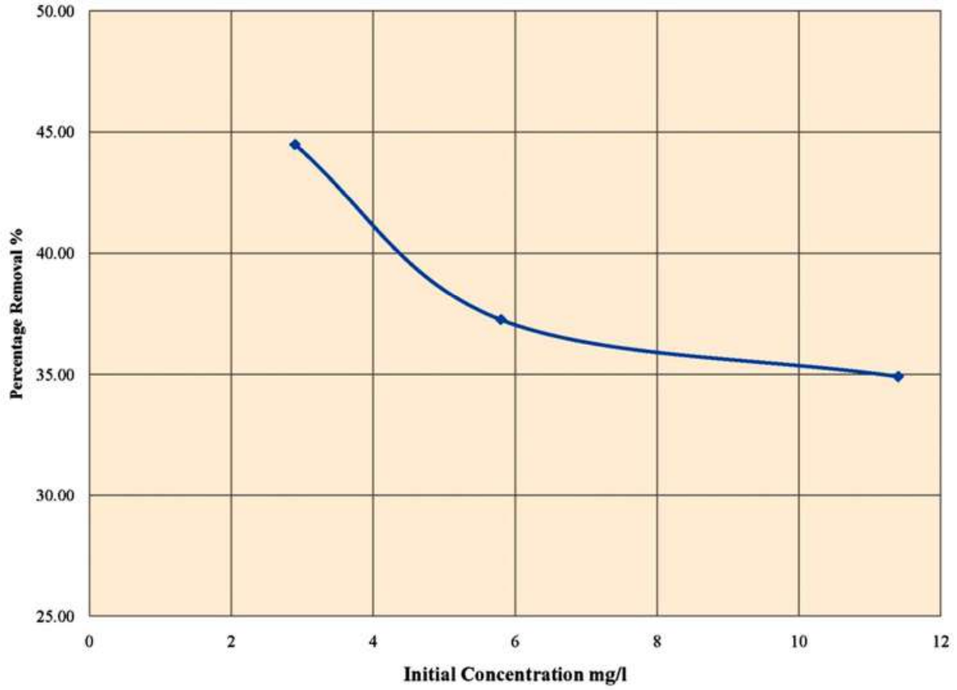


Figure 4-23 Effect of initial concentration in removal for real wastewater samples

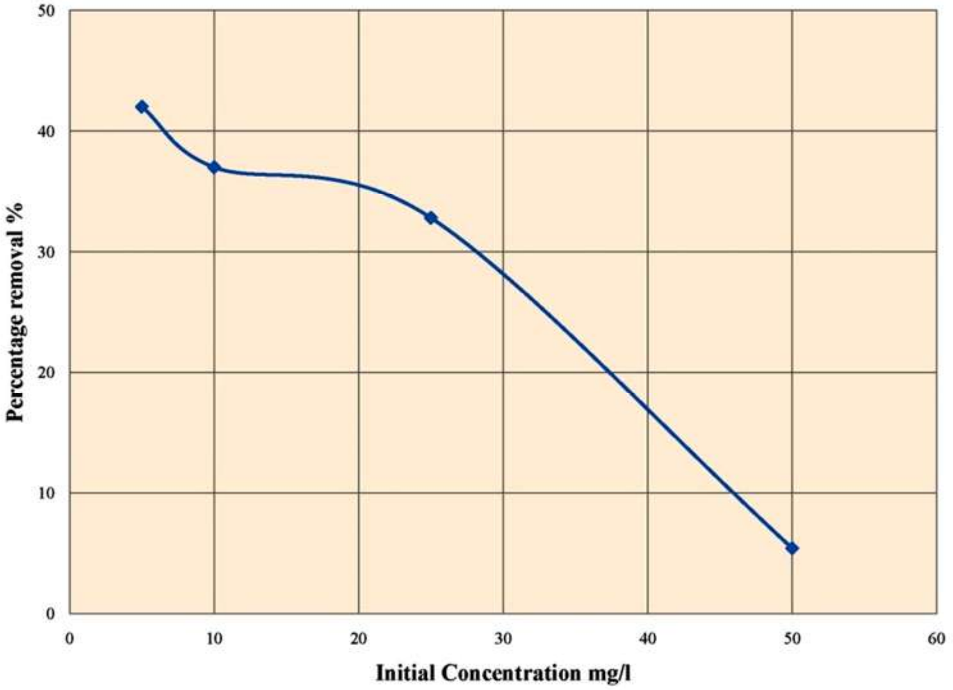


Figure 4-24 Effect of initial concentration in removal for Synthetic wastewater samples (LAS)

It was very difficult to find out a real sample of wastewater with initial concentration greater than 11.4 mg/l, and the efforts to add LAS to a real wastewater to increase the concentration faced with unjustified behavior of the real wastewater samples. In addition, the condition of the experiments will not be similar.

From the similarity between the two behaviors of LAS at synthetic solution and detergent at real wastewater, it can be concluded that the other existing substances in the real wastewater has a minimal effect on the removal of detergent from wastewater in general.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 Conclusion regarding activated carbon production

It can be concluded from the research that:

- Activated carbon can be produced from crushed olive seeds under a carbonization temperature of 500 ^{o}C and a constant flow of nitrogen 400 to 500 cm^3/min, and activated by microwave with the assistance of KOH 1:2 w/w within 20 minutes.
- The produced activated carbon has a high surface area 540 m2/g and can compete the commercial types used in water treatment.
- Crushed Olive's seeds, source of environment contamination, can be converted to a friendly environment material of economical and technical value.

5.1.2 Conclusion regarding detergent removal by activated carbon

- Detergent can be removed by activated carbon through adsorption process in both synthetic solution and real wastewater with a considerable affeciency .
- The removal of LAS from synthetic solution is affected by the contact time positively as in the first 20 hours 35% of the 10 mg LAS/l concentration is removed and at equilibrium (5days) 98% of the LAS was removed.
- pH within the range of 5 to 9 has no significant effect on the percentage removal of detergent, and this support the use of the activated carbon in removing of detergent from wastewater which typically has a pH within this range.
- Initial LAS concentration within the range of 5 to 25 mg/l has minimal effect on the removal at equilibrium stage, while at the range greater than 25 to 200 mg/l a significant effect is clear as the removal efficiency dropped from 98% to 65%.
- Percentage removal increases by the increase of the adsorbent (AC) quantity, however, the amount adsorbed by unit mass decreases.
- It is found that Freundlich isotherm describes detergents adsorption process in the range of 5 to 25 mg LAS/l concentration while Langmuir isotherm describe

that relation at the range of 25 to 50 and 50 to 200 mg/l respectively at room temperature (20 to 25 °C and 6.67 pH.

- Results from the isotherms prove that LAS is favorable for removal by activated carbon from aqueous solutions.
- Produced activated carbon can remove detergent from real wastewater as efficient as it removes it from the synthetic samples. The percentage removal of detergent from real wastewater reach 44.5% at low concentrations (2.9 mg/l), while at high concentrations, (11.4 mg/l) the percentage removal dropped to 35%.
- Existing organic substances in the real wastewater has no significant effect on the removal of detergent from wastewater. Organic matters and organic nitrogen concentrations dropped from 193 and 56.1 to 171 and 42.3 respectively, when 1 gram of activated carbon was added to wastewater samples with a contact time of 20 hours.

5.2 Recommendations

- Since activated carbon produced from olives crushed seeds is technically and financially efficient and contributes in environmental protection, it is recommended to produce it from olives crushed seeds as a replacement of commercial activated carbon.
- Since the produced activated carbon can efficiently remove detergents, it is recommended to use it in reducing detergents concentration from treated wastewater (especially in Gaza wastewater treatment plants) for reuse purposes.
- It is recommended to support the researches centers in Gaza strip, to allow the researchers to run their researches as per the international standards with suitable equipments.

5.3 Further Studies and Research

- Further study is suggested to investigate the possibility of producing activated carbon from local raw materials such as agricultural waste such as Tomato, Cucumbers and potato plants.

- Further study is required to improve the produced activated carbon from organic materials resulted from agricultural sector and find out the best granular size of the carbon, best procedure for carbonization and activation.
- Further study on column experiments is required to find out some design characteristics of the activated carbon such as Empty Bed Contact Time (EBCT), Specific throughput (ST), Carbon usage rate (CUR), Mass of organic material adsorbed at breakthrough and Time to breakthrough that will help in the practical use of the activated carbon in wastewater treatment.

REFERENCES

Aboulhassan, M. A., Souabi, S., & Yaacoubi, A. (2006). Removal of surfactant from industrial wastewaters by coagulation flocculation process. *Int. J. Environ. Sci. Tech.* , Vol.3 PP 327-332.

Abu Madi, M., Braadbaart, O., & Al-Sa'ed, R. (2003). Willingness of farmers to pay for reclaimed wastewater in Jordan and Tunisia. *Water Science and Technology: Water Supply* , Vol 3 No 4 pp 115–122.

Abu-Zreig, M., Rudra, R. P., & Dickinson, W. T. (2003). Effect of Application of Surfactants on Hydraulic Properties of Soils. *Biosystems Engineering ,* Vol. 84 PP 363–372.

Alau, K. K., Gimba, C. E., & Kagbu, J. A. (2010). Removal of Dyes from Aqueous Solution Using Neem (Azadirachta Indica) Husk as Activated Carbon. *scholars resrearchs library* , Vol. 2 PP 456-461.

Aljundi, I. H., & Jarrah, N. (2008). A study of characteristics of activated carbon produced from Jordanian olive cake. *Analytical and applied pyrolyses ,* Vols. 81 PP 33–36.

Almasri, M. N., & McNeill, L. S. (2008). Optimal planning of wastewater reuse using the suitability approach: A conceptual framework for the West Bank,Palestine. *Desalination* , Vol 248 PP 428–435.

Ashour, F. (2011). The Sanitation Situation in the Gaza Strip, Problems and Solutions. Gaza: Islamic University - Engineering Club.

Associatidn-SAD. (1994). *Soaps and Detergents.* Washington, DC: The Soap and Detergents Association.

ASTM. (1999). Standard Test Methods for Carbon BlackÐSurface Area by Multipoint B.E.T. Nitrogen Adsorption. Barr Harbor Drive - West Conshohocken, PA: ASTM Committee on Standards.

Baccar, R., Bouzid, J., Feki, M., & Montiel, A. (2008). Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. *Journal of Hazardous Materials* , Vols. 162 PP 1522–1529.

Becagli, S., Ghedini, C., & Peeters, S. (2011). MBAS (Methylene Blue Active Substances) and LAS (Linear Alkylbenzene Sulphonates) in Mediterranean coastal aerosols: Sources and transport processes. *Atmospheric Environment* , Vols 45 PP 6788-6801.

Behler, A. (2008). Surfactants Based on Renewableresources for personal care and Hope Care. *CareChemicals - Cognis* . Munich.

Bla´zquez, G., Herna´inz, F., Calero, M., & Ruiz-Nu´n˜ez, L. F. (2004). Removal of cadmium ions with olive stones: he effect of somes parameters. *Process Biochemistry* , Vols. 40 PP 2649–2654.

Branislav, J. R. (2010). The effect of detergent as polluting agent on the photosynthetic activity and chlorophyll content in bean leaves. *Health* , Vol.2, PP 395-399.

CEFIC. (April 86). Test Methods. *Conseil Europeen des Federations de l'lndustrie chimique* . Europian Councel of Chemical manufacturers Federations.

Chen, H., & Hashisho, Z. (2012). Effects of microwave activation conditions on the properties of activated oil sands coke. *Fuel Processing Technology ,* Vols. 102 PP 102-109.

CMWU. (2007). Databases of the Coastal Municipal Water Utility. Gaza: CMWU.

CMWU. (2008). *Water Status in Gaza Strip.* Gaza: CMWU.

Cruz, G., Pirla, M., Huuhtanen, M., Carrion, L., Alvarenga, E., & Ritta, L. (2012). Production of Activated Carbon from Cocoa (Theobroma cacao) Pod Husk. *Civil Environment Engg , 2* (2), Vol. 2.

Demiral, H., Demiral, I., Karabacakoglu, B., & Tümsek, F. (2011). Production of activated carbon from olive bagasse by physical activation. *Chemical Engineering Research and Design ,* Vols. 89 PP 206-213.

Deng, H., Li, G., Yang, H., Tang, J., & Tang, J. (2010). Preparation of activated carbons from cotton stalk by microwave assisted KOH and K 2 CO 3 activation. *Chemical Engineering Journal ,* Vols. 136 PP 373-381.

Deng, H., Li, G., Yang, H., Tang, J., & Tang, J. (2010). Preparation of activated carbons from cotton stalk by microwave assisted KOH and K 2 CO3 activation. *Chemical Engineering Journal ,* Vols. 163 PP 373-381.

Deng, H., Yang, L., Tao, G., & Dai, J. (2008). Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation—Application in methylene blue adsorption from aqueous solution. *Journal of Hazardous Materials ,* Vols. 166 PP 1514–1521.

El-Hamouz, A., Hilal, H. S., Nassar, N., & Mardawi, Z. (2006). Solid olive waste in environmental cleanup: Oil recovery and carbon production for water purification. *Journal of Environmental Management ,* Vols. 84 PP 83–92.

El-Said, S. M. (2004). Adsorptive Removal of some Detergents from Wastewater using Friendly Environmental Material. *Ass. Univ. Bull. Environ.* , Vol. 7 No. 2.

El-Sheikh, A. H., Newman, A. P., Al-Daffaee, H. K., Phull, S., & Cresswell, N. (2003). Characterization of activated carbon prepared from a single cultivar of Jordanian Olive stones by chemical and physicochemical techniques. *J. Anal. Appl. Pyrolysis ,* Vols. 71 PP 151–164.

FAO. (2012). *Coping with water scarcity: An action framework for agriculture and food security.* Rome: Food and Agriculture Organization of the United Nations.

Farlex. (2013, Jan. 20). *Encyclopedia*. Retrieved Jan. 20, 2013, from The free dictionary by Farlex: http://encyclopedia.thefreedictionary.com/Steric+interaction

Fatta, D., & Alaton, A. (2005). Wastewater Reuse: Problems and Challenges in Cyprus, Turky, Jordan, and Morocco. *EWRA Europian Water , Vols.11 PP 63 - 69*,

Foo, K. Y., & Hameed, B. H. (Dec-2011). Coconut husk derived activated carbon via microwave induced activation: Effects of activation agents, preparation parameters and adsorption performance. *Chemical Engineering Journal ,* Vols. 184 PP 57-65.

Foo, K. Y., & Hameed, B. H. (April-2011). Preparation and characterization of activated carbon from pistachio nut shells via microwave-induced chemical activation. *Biomass and Bioenergy* , Vols. 35 PP 3257-3261.

Foo, K. Y., & Hameed, B. H. (May-2011). Preparation and characterization of activated carbon from pistachio nut shells via microwave-induced chemicalactivation. *Biomass and Bioenergy ,* Vols. 35 PP 3257-3261.

Foo, K. Y., & Hameed, B. H. (Feb-2011). Preparation of activated carbon from date stones by microwave induced chemical activation: Application for methylene blue adsorption. *Chemical Engineering Juornal ,* Vols. 170 PP 338-341.

Grassi, M., Kaykioglu, G., Belgiorno, V., & Lofrano, G. (2012). *Emerging Compounds Removal from Wastewater* (Vol. I). Springer.

Gueu, S., Yao, B., Adouby, K., & Ado, G. (2006). Heavy Metals removal in Aqueous Solution by activated Carbons prepared from Coconut Shell and Seed Shell of Palm Tree. *Journal of Applies Sciences ,* Vols. 6 PP 2789 - 2793.

Hakan, D., Ilknur, D., & Belgin, K. (2011). Production of activated carbon from olive bagasse by physical activation. *Chemical Engineering Research and Design ,* Vols. 89 PP 206–213.

Hamdan, S., Nassar, A., & Troeger, U. (2011, January 01). Impact on Gaza aquifer from recharge with partially treated wastewater. *Journal of Water Reuse and Desalination* , pp. 36-44.

Hernández-Montoy, V., García-Servin, J., & Bueno-López, J. I. (2012). *Thermal Treatments and Activation Procedures Used in the Preparation of Activated Carbons, Lignocellulosic Precursors Used inthe Synthesis of Activated Carbon - Characterization Techniques and Applications in the WastewaterTreatment* (Vol. I). México: InTech.

Ho, Y. S., Ng, J. C., & McKay, G. (2001). Removal of Lead (II) from effluents by sorption on peat using second order Kinatics. *Separation Science and Technology ,* Vols. 36 PP 241–261.

Hosseinnia, A., Hashtroudi, M. S., & Banifatem, M. (2007). The Use of Rice Husk to Remove Wastewater Surfactants. *Water & Wastewater Asia* .

Husseien, M., A.Amer, A., El Mughraby, A., & A. Taha, N. (2007). Utilization of Barley Straw as a Source of a Activated Carbon for Removal of Methylene Blue from Aqueous Solution. *Journal of Applied Sciences Research* , Vols. 3 PP1352-1358.

Intini, F., Kühtz, S., & Rospi, G. (2011). Energy Recovery of the Solid Waste of the Olive Oil Industries LCA Analysis and Carbon Footprint Assessment. *Journal of Sustainable Energy & Environment* , Vols. 2 PP 157 - 166.

IUPAC. (2012). Compendium of Chemical Terminology - Gold Book. *International Union of Pure and Applied Chemistry* , Vol. Version 2.3.2.

Ji, Y., Li, T., Zhu, L., Wang, X., & Lin, Q. (2007). Preparation of activated carbons by microwave heating KOH activation. *Applied Surface Science* , Vols. 254 PP 506–512.

KEMI. (2003). *Information on Substances*. Retrieved April 20, 2013, from KEMI, Swedish Chemical Agency: http://apps.kemi.se/flodessok/floden/kemamne_Eng/LAS_eng.htm

Kittani, H. (2008). Towards A Comprehensive Treated Wastewater Reuse Strategy. *Birzeit Water Drop - Year of Sanitation* (pp. 23-33). Birzeit: Birzeit University.

Kostas, A., Valet, N., Spiratos, D., & Siragakis, G. (2006). Olive oil and pomace olive oil processing. *Grasas Y Acetites* Vols. 57 PP 56-67.

Kroontje, W., Judy, J. N., & Hahne, H. C. (1973). Effect of Detergent-Laden Water on the Growth of Corn. Department of Agronomy. Virginia Polytechnic Institute and State University, Blacksburg, Virginia: Virginia Water Resources Research Center.

Kula, I., Ugurlu, M., Karaoglu, H., & Celik, A. (2007). Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by ZnCl2 activation. *Bioresource Technology* , Vols. 99 PP 492–501.

Li, W., Zhang, L.-b., Peng, J.-h., Li, N., & Zhu, X.-y. (2007). Preparation of high surface area activated carbons from tobacco stems with K 2 CO 3 activation using microwave radiation. *Industrial Crops and Products* , Vols. 27 PP 341 - 347.

Liu, Q.-S., Zheng, T., Wang, P., & Guo, L. (2009). Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation. *Industrial Crops and Products ,* Vols. 31 PP 233–238.

Mahavi, A. H., Vaezi, F., & Alavi, N. (2004). Evaluation GAC for Detergant Removal from Secondary Effluent Ghods WWTP. *Pakistan Journal of Biological science ,Vols.* 7 PP 2121-2124.

Malik, R., Ramteke, D. S., & Wate, S. R. (2006). physico-Chemicaland surface characterization of adsorbent prepared from groundnut shell by ZnCl2 activation and its ability to adsorb colour. *Journal of chemical technology ,* Vols. 13 pp 319-328.

Mansalvo, M. M., Mohedano, A. F., & Rodriguez, J. J. (2011). Activated carbons from sewage sludge Application to aqueous-phase adsorption of 4chlorophenol. *adesalination* Vols. 277 PP 377 - 382.

Mansooreh, S., & Kaghazchi, T. (2008). Adsorption of gold ions from industrial wastewater using activated carbon derived from hard shell of apricot stones – An agricultural waste. *Bioresource Technology ,* Vols. 99 PP 5374-5383.

Mart´ınez, M. L., Torres, M. M., Guzm´an, C. A., & Maestri, D. M. (2005). Preparation and characteristics of activated carbon from olive stones and walnut shells. *ndustrial Crops and Products ,* Vols. 23 PP 23–28.

McNeill, S. L., Almasri, N. M., & Mizyed, N. (2008). A sustainable approach for reusing treated wastewater in agricultural irrigation in the West Bank – Palestine. *Desalination ,* Vols.251 PP 315–321.

Mogheir, Y., & et-al. (2007). *Treated Wastewater Reuse in Palestine.* Gaza.

Moreno-Castilla, C., Carrasco-Marin, F., Carrasco-Marın, F., Lopez-Ramon, M. V., & Alvarez-Merino, M. A. (2000). Chemical and physical activation of olive-mill waste water to produce activated carbons. *Carbon* Vols. 39 PP 1415–1420.

Munusamy, K., Somany, R. S., & Bajaj, H. C. (2011). Tamarind Seeds Carbon: preparation and Methane Uptake. *BioResources ,* Vols. 6 PP 537-551.

Myers, D. (2006). *Surfactant science and technology* (Vol. Third ed). Hoboken, N.J: Willey.

OLIVAE. (2012). International Olive Council. *Official magazine of the International Olive Council , 117* . Madeid Spain: Produced by Advantia, S.A.

Orkide, M., Meral, Ö., & Özdemi, E. (2009). Detergent and phosphate pollution ın Gediz River,Turky. *Academic Journals* Vols. 8 PP 3568-3575.

PCBC. (2012). *Survey of Olives Mills in Palestine.* Ramallah - Palestine: PCBC.

Rabah, F. (2010). Water Treatment Technology, Water Resources Engineering lectures. *Water treatment lectures* . Gaza: Islamic University - Gaza.

Rebhun, M., & Streit, S. (1973). Physco-Chemical Treatment of Strong Municipal Wastewater. *Water Reserch* Vols. 8 PP 195 - 201.

Rodrıguez, G., Antonio Lama, A., Rodrıguez, R., Jime´ne, A., Guille´n, R., & Ferna´ndez-Bolan˜os, J. (2007). Olive stone an attractive source of bioactive and valuable compounds. *Bioresource Technology* Vols. 99 PP 5261–5269.

Saravanane, R., Sundararajan, T., & Sivamurthy Reddy, S. (2001). Chemically modified low cost treatment for heavy metal effluent management. *Environmental Management and Health* ,Vols. 12 PP 215 - 224.

Shomar, B., Muller, G., & Yahya, A. (2004). Potential use of treated wastewater and sludge in the agricultural sector at Gaza Strip. *Clean Techn Environ Policy ,Vols. 6 PP* 128–137.

Spahis, N., Addoun, A., Mahmoudi, H., & Ghaffour, N. (2007). Purification of water by activated carbon prepared from olive stones. *Desalination , V*ols. 222 PP 519–527.

Stavropoulos, G. G., & Zabaniotou, A. A. (2005). Production and characterization of activated carbons from olive-seed waste residue. *Microporous and Mesoporous Materials* , Vols. 82 PP 79–85.

Ubago-Pe´rez, R., Carrasco-Marı´n, F., Faire´n-Jime´nez, D., & Moreno-Castilla, C. (2006). Granular and monolithic activated carbons from KOH-activation of olive stones. *Microporous and Mesoporous Materials ,* Vols. 92 PP 64–70.

UNDP. (2008). *The Olive Harvesting in the West Bank and Gaza.* Ramallah: United Nations Development Programme.

Viswanathan, B., Indra Neel, P., & Varadaraja, T. K. (2009). *Methods of Activation and Specific Applications of Carbon Materials* (Vol. I). Madras: National Centre for Catalysis Research.

Viswanathan, B., Indra Neel, P., & Varadaraja, T. K. (2009). *Methods of Activation and Specific Applications of Carbon Materials.* India: National Centre for Catalysis Research.

Weber, W. J. (1974). *IUPAC.* Retrieved May 03, 2013, from old.iupac.org/: http://pac.iupac.org/publications/pac/pdf/1974/pdf/3703x0375.pdf

Wikipedia-Detergent. (2012). *Detergents.* Retrieved October 18, 2012, from Wikipedia the Free Encyclobedia: http://en.wikipedia.org/wiki/Detergent

Wikipedia-Soap. (2012, October 15). *Wikipedia.* Retrieved October 16, 2012, from Wikipedia the free Encyclopedia: http://en.wikipedia.org/wiki/Soap

Wikipedia-surfactant. (2012). *Surfactant.* Retrieved Nov. 03, 2012, from Wikipedia: http://en.wikipedia.org/wiki/Surfactant

World-Bank. (2007). *Making the most scarcity Accountability forbetter water managementin the Middle East and North africa.* Washington DC: The International Bank for Reconstruction and Development / The World Bank.

World-Bank. (2009). *West Bank and Gaza Assessment of Restrictions on PalestinianWater Sector Development.* Washington DC: The International Bank for Reconstruction and Development/The World Bank.

world-Bank. (2004). *West Bank and Gaza Wastewater Treatment and Reuse Policy Note.* Washngton DC: Documents of the World Bank.

Xiaoge, C., Jeyaseelan, S., & Graham, N. (2002). Physical and chemical properties study of the activated carbon made from sewage sludge. *Waste Management ,* Vols. 22 PP 755-760.

Yagmur, E., Ozmak, M., & Aktas, Z. (2008). A novel method for production of activated carbon from waste tea by chemical activation with microwave energy. *Fuel ,* Vols. 87 PP 3278–3285.

Yeddou, A. R., Nadjemi, B., Halet, F., Ould-Dris, A., & Capart, R. (2009). Removal of cyanide in aqueous solution by oxidation with hydrogen peroxide in presence of activated carbon prepared from olive stones. *Minerals Engineering ,* Vols. 23 PP 32–39.

Ying, G.-G. (2006). Fate, behavior and effects of surfactants and their degradation products in the environment. *Environment International ,* Vols. 32 PP 417 – 431.

Zaharaki, D., & Komnitsas, K. (2009). *Existing and emerging technologies for the treatment of olive oil mill wastewater.* Hania, Greece: Department of Mineral Resources Engineering, Technical University of Crete.

APPENDICES

Appendix A: Calculation

Table A.1: Acetic acid, Commercial Activated Carbon Isotherm calculation

Sample No	C_0	Acid volume	Titration NaOH Volume				C_e	C_0-C_e	N	C_e/N
			A	B	C	Av. Vol.				
	M	ml	ml	ml	ml	ml	M	M		
1	0.0174	50	6.15	6.01	6.04	6.067	0.0098	0.0076	0.0008	12.98
2	0.0436	25	9.12	9.06	9.08	9.087	0.0294	0.0142	0.0014	20.79
3	0.061	20	10.8	10.6	10.51	10.637	0.0431	0.0179	0.0018	24.04
4	0.078	10	6.94	7.05	7.16	7.050	0.0571	0.0209	0.0021	27.33
5	0.0958	10	8.93	8.93	8.95	8.937	0.0724	0.0234	0.0023	30.92
6	0.13	10	12.8	12.66	12.78	12.747	0.1032	0.0268	0.0027	38.59
7	0.174	10	16.64	17.2	17.48	17.107	0.1386	0.0354	0.0035	39.10

Note: Concentration of NaOH used for titration is 0.081 mol/L

$C_e/N = C_e *(1/N_m) + (1/K_L) * (1/N_m)$

Avogadro's No	=	6.02E+23	molecule/mole
Acetic Acid Molecule	**=**	2.1E-19	m^2/molecule
From Chart ($1/N_m$)	=	**205.4**	
N_m	=	**0.004869**	
K_L	=	**14.30362**	
Surface area	=	**615.482**	m^2/g

Surface area from the Manufacturer sheet by BET N_2 test is 1100 m^2/g

Correction Factor = 1100/615 = 1.788

The factor will be taken to correct the surface area measured by acetic acid will be taken as **1.7**

Table A.2: Acetic acid, Produced Activated Carbon, Time of activation 5 minutes

Sample No	C_0	C_e	C_0-C_e	N	C_e/N
	M	M	M		
1	0.0150	0.0100	0.0050	0.0005	20.00
2	0.0375	0.0260	0.0115	0.0012	22.61
3	0.0700	0.0530	0.0170	0.0017	31.18
4	0.0950	0.0810	0.0140	0.0014	57.86
5	0.1270	0.1120	0.0150	0.0015	74.67
6	0.1600	0.1420	0.0180	0.0018	78.89

From Chart ($1/N_m$) = **507 from Chart**

1/KL) * (1/Nm) = **11.67 from Chart**

N_m = 0.001972

K_L = **43.44473**

Surface area (Acetic Acid) = **249.3491** m^2/g

Correction Factor for BET N_2 = 1.7

Surface area = **423.89** m^2/g

Table A.3: Acetic acid, Produced Activated Carbon, Time of activation 10 minutes

Sample No	**C_0**	**C_e**	**C_0-C_e**	**N**	**C_e/N**
	M	M	M		
1	0.015	0.01	0.0050	0.0005	20.00
2	0.0375	0.025	0.0125	0.0013	20.00
3	0.07	0.055	0.0150	0.0015	36.67
4	0.095	0.08	0.0150	0.0015	53.33
5	0.127	0.11	0.0170	0.0017	64.71
6	0.16	0.142	0.0180	0.0018	78.89

From Chart ($1/N_m$) = **475 from Chart**

1/KL) * (1/Nm) = **12.12 from Chart**

N_m = 0.002105

K_L = **39.19142**

Surface area (Acetic Acid) = **266.1474** m^2/g

Correction Factor for BET N_2 = 1.7

Surface area = **452.451** m^2/g

Table A.4: Acetic acid, Produced Activated Carbon, Time of activation 15 minutes

Sample No	**C_0**	**C_e**	**C_0-C_e**	**N**	**C_e/N**
	M	M	M		
1	0.0162	0.0075	0.0087	0.0009	8.62
2	0.0287	0.0225	0.0062	0.0006	36.29
3	0.0625	0.0525	0.0100	0.0010	52.50
	0.1	0.085	0.0150	0.0015	56.67
5	0.1275	0.11	0.0175	0.0018	62.86
6	0.1625	0.1425	0.0200	0.0020	71.25

From Chart ($1/N_m$) = **394 from Chart**

1/KL) * (1/Nm) = **20.4 from Chart**

N_m = 0.002538

K_L = **19.3137**

Surface area (Acetic Acid) = **320.863** m^2/g

Correction Factor for BET N_2 = 1.7

Surface area = **545.5** m^2/g

Table A.5: Acetic acid, Produced Activated Carbon, Time of activation 25 minutes

Sample No	C_0	C_e	C_0-C_e	N	C_e/N
	M	M	M		
1	0.016	0.010	0.0062	0.0006	16.13
2	0.034	0.022	0.0117	0.0012	18.80
3	0.063	0.051	0.0115	0.0012	44.35
4	0.093	0.080	0.0125	0.0013	64.00
5	0.127	0.110	0.0170	0.0017	64.71
6	0.163	0.140	0.0225	0.0023	62.22

From Chart (1/N_m) = **403 from Chart**

1/KL) * (1/Nm) = **18 from Chart**

N_m = 0.002481

K_L = **22.388**

Surface area (Acetic Acid) = **313.697** m^2/g

Correction Factor for BET N_2 = 1.7

Surface area = **533.285** m^2/g

Table A.6: Acetic acid, Produced Activated Carbon, Time of activation 35 minutes

Sample No	C_0	C_e	C_0-C_e	N	C_e/N
	M	M	M		
1	0.016	0.009	0.0075	0.0007	11.74
2	0.034	0.024	0.0100	0.0010	23.87
3	0.063	0.050	0.0125	0.0013	40.00
4	0.093	0.080	0.0125	0.0013	64.00
5	0.127	0.113	0.0145	0.0015	77.59
6	0.163	0.137	0.0255	0.0026	53.73

From Chart (1/N_m) = **406 from Chart**

1/KL) * (1/Nm) = **18.1 from Chart**

N_m = 0.00244

K_L = **22.9834**

Surface area (Acetic Acid) = **303.894** m^2/g

Correction Factor for BET N_2 = 1.7

Surface area = **516.62** m^2/g

Table A.7: Sample from all the activated char at 20 min

Sample No	**C_0**	**C_e**	**C_0-C_e**	**N**	**C_e/N**
	M	M	M		
1	0.0156	0.009	0.0066	0.0007	13.64
2	0.0342	0.022	0.0127	0.0013	16.93
3	0.0720	0.049	0.0230	0.0023	21.30
4	0.0950	0.076	0.0190	0.0019	40.00
5	0.1320	0.112	0.0200	0.0020	56.00
6	0.1650	0.142	0.0230	0.0023	61.74

From Chart ($1/N_m$) = **393.4 from Chart**

1/KL) * (1/Nm) = **8.801from Chart**

N_m = 0.00254

K_L = **49.67**

Surface area (Acetic Acid) = **321.35** m^2/g

Correction Factor for BET N_2 = 1.7

Surface area = **546.3** m^2/g

Table A.8: Freundlich isotherm for LAS adsorption onto produced Activated Carbon (Co from 5 to 25 mg/l)

Sample No	**C_0**	**C_e**	**C_0-C_e**	**m**	**X/m**	**C_e/(x/m)**	log C_e	log X/m
	mglVl	mg/l	mg/l	g				
1	5	0.1960	4.8040	1.0000	0.2402	0.82	-0.70774	-0.61943
2	10	0.2100	9.7900	1.0000	0.4895	0.43	-0.67778	-0.31025
3	15	0.2400	14.7600	1.0000	0.7380	0.33	-0.61979	-0.13194

4	20	0.3280	19.6720	1.0000	0.9836	0.33	-0.48413	-0.00718
5	25	0.3480	24.6520	1.0000	1.2326	0.28	-0.45842	0.090822

log Kf = 1.14

1/n = 2.27

n = 0.441

K_f = 3.127

$$\mathbf{X/M = 3.127\ C_e^{2.27}}$$

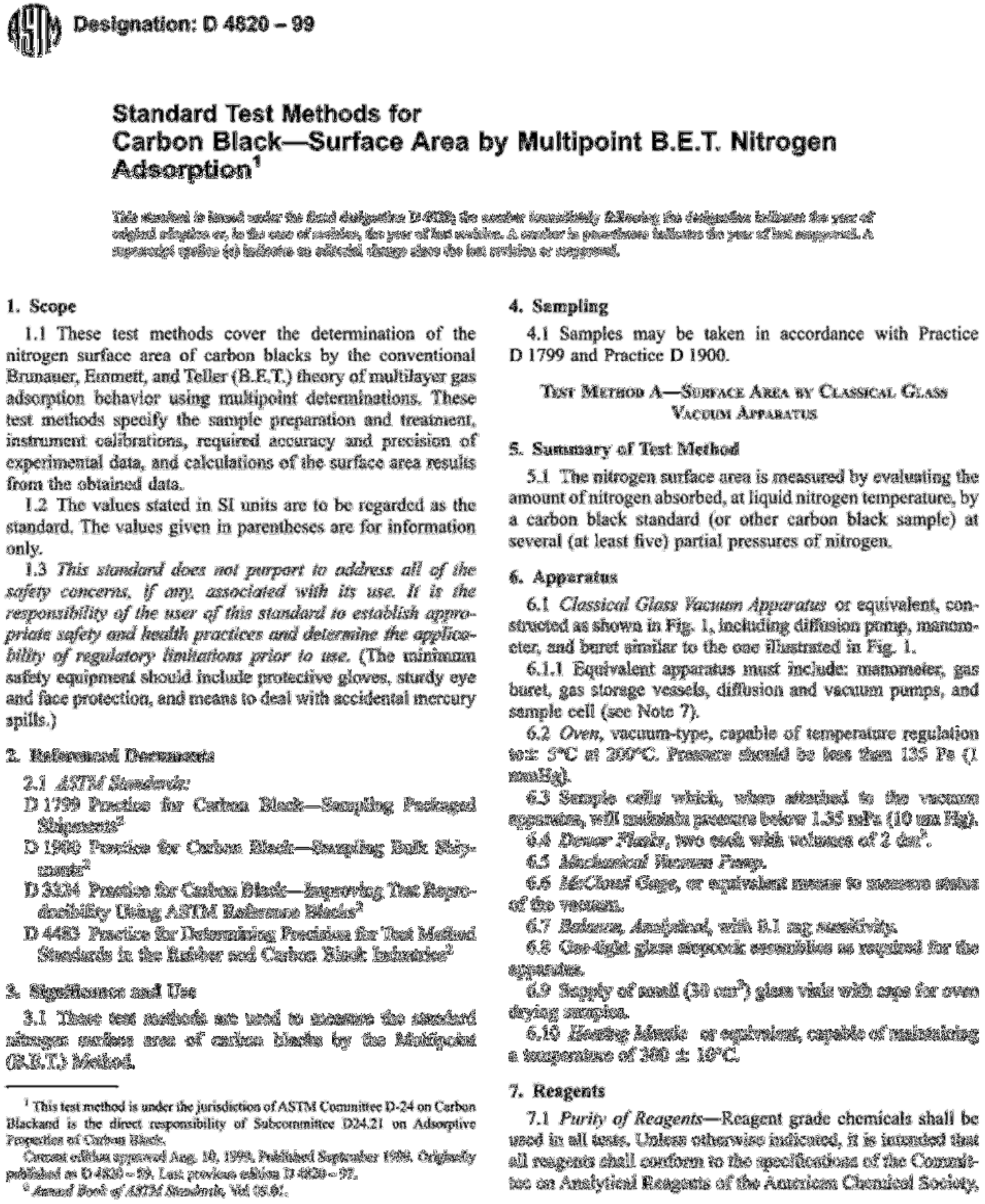
Table A.9: Langmuir isotherm for LAS adsorption onto produced Activated Carbon (C_o from 50 to 200 mg/l)

Sample No	C_0	C_e	m	m	C_0-C_e	N	C_e/N
	M	M	g	l	M		
3	50	12.0000	1.0000	0.0500	38.0000	1.9000	6.32
4	100	25.5000	1.0000	0.0500	74.5000	3.7250	6.85
5	200	70.5700	1.0000	0.0500	129.4300	6.4715	10.90

slope = 0.081
1/ab = 5.093
ab = 0.196
1/a = 0.081
a = 12.346
b = 0.016

$$X/M = 0.196\ C_e / (1+ 0.016C_e)$$

Appendix B: Standard Test Methods for Carbon Black Surface Area by Multipoint B.E.T. Nitrogen Adsorption



Designation: D 4820 – 99

Standard Test Methods for Carbon Black—Surface Area by Multipoint B.E.T. Nitrogen Adsorption[1]

This standard is issued under the fixed designation D 4820; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the determination of the nitrogen surface area of carbon blacks by the conventional Brunauer, Emmett, and Teller (B.E.T.) theory of multilayer gas adsorption behavior using multipoint determinations. These test methods specify the sample preparation and treatment, instrument calibrations, required accuracy and precision of experimental data, and calculations of the surface area results from the obtained data.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* (The minimum safety equipment should include protective gloves, sturdy eye and face protection, and means to deal with accidental mercury spills.)

2. Referenced Documents

2.1 *ASTM Standards:*

D 1799 Practice for Carbon Black—Sampling Packaged Shipments[2]

D 1900 Practice for Carbon Black—Sampling Bulk Shipments[2]

D 3324 Practice for Carbon Black—Improving Test Reproducibility Using ASTM Reference Blacks[2]

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[2]

3. Significance and Use

3.1 These test methods are used to measure the standard nitrogen surface area of carbon blacks by the Multipoint (B.E.T.) Method.

4. Sampling

4.1 Samples may be taken in accordance with Practice D 1799 and Practice D 1900.

TEST METHOD A—SURFACE AREA BY CLASSICAL GLASS VACUUM APPARATUS

5. Summary of Test Method

5.1 The nitrogen surface area is measured by evaluating the amount of nitrogen absorbed, at liquid nitrogen temperature, by a carbon black standard (or other carbon black sample) at several (at least five) partial pressures of nitrogen.

6. Apparatus

6.1 *Classical Glass Vacuum Apparatus* or equivalent, constructed as shown in Fig. 1, including diffusion pump, manometer, and buret similar to the one illustrated in Fig. 1.

6.1.1 Equivalent apparatus must include: manometer, gas buret, gas storage vessels, diffusion and vacuum pumps, and sample cell (see Note 7).

6.2 *Oven*, vacuum-type, capable of temperature regulation to ± 5°C at 200°C. Pressure should be less than 135 Pa (1 mmHg).

6.3 Sample cells which, when attached to the vacuum apparatus, will maintain pressure below 1.35 mPa (10 μm Hg).

6.4 *Dewar Flasks*, two each with volumes of 2 dm^3.

6.5 *Mechanical Vacuum Pump.*

6.6 *McLeod Gage*, or equivalent means to measure status of the vacuum.

6.7 *Balance, Analytical*, with 0.1 mg sensitivity.

6.8 Gas-tight glass stopcock assemblies as required for the apparatus.

6.9 Supply of small (30 cm^3) glass vials with caps for oven drying samples.

6.10 *Heating Mantle* or equivalent, capable of maintaining a temperature of 300 ± 10°C.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,

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[1] This test method is under the jurisdiction of ASTM Committee D-24 on Carbon Blackand is the direct responsibility of Subcommittee D24.21 on Adsorptive Properties of Carbon Black.

Current edition approved Aug. 10, 1999. Published September 1999. Originally published as D 4820 – 88. Last previous edition D 4820 – 97.

[2] *Annual Book of ASTM Standards*, Vol 09.01.

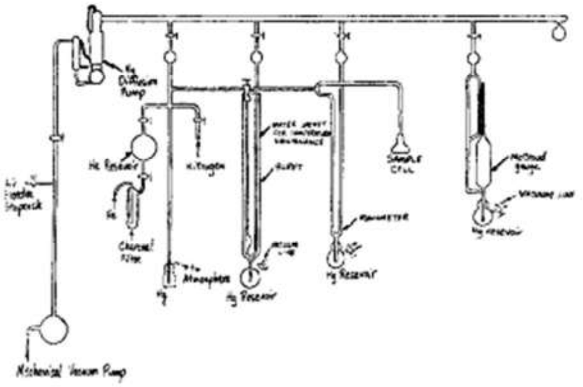

FIG. 1 Glass Vacuum Apparatus

where such specifications are available.[3] Other grades may be used, provided it is first ascertained that it is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity.

7.3 *Liquid nitrogen*.

7.4 Ultra-high purity nitrogen gas, cylinder, or other source of prepurified nitrogen gas.

7.5 Ultra-high purity helium gas, cylinder, or other source of prepurified helium gas.

7.6 *Instrument grade mercury*.

7.7 High vacuum stopcock grease, Apiezon-type *N*.

8. Preparation of Apparatus

NOTE 1—This procedure only need be performed for the initial calibration of the gas buret or when a modification is made to the gas buret.

8.1 Zero the manometer by evacuating both arms of the manometer to a pressure below 1.35 mPa (10 nmHg) and adjusting the height of the mercury columns to the same zero reading in both arms.

8.2 *Determine Gas Buret Constant*:

8.2.1 Install a sample cell of approximately 30 cm ^{3} volume on the sample cell position of the apparatus assuring no vacuum leaks.

8.2.2 Evacuate the sample cell, manometer, and gas buret to a pressure below 1.35 mPa (10 nmHg).

8.2.3 Immerse the sample cell in a water-ice bath contained in a Dewar flask such that the entire sample bulb is covered.

8.2.4 Fill the gas buret to approximately 50 % of its capacity with helium.

8.2.5 Obtain initial gas buret volume and temperature—V_{B1}, T_{B1} (K).

8.2.6 Transfer approximately 2 cm^3 of helium to the sample cell.

8.2.7 Read and record the gas buret level and temperature after helium dosing—V_{B2}, T_{B2} (K).

8.2.8 Read and record the pressure in the sample cell after dosing (P_c); and the sample cell temperature, that is, ice-bath temperature T_c (K).

8.2.9 Repeat 8.2.5-8.2.8 at least two times to obtain a total of three data sets.

8.2.10 Remove the sample cell and fill the sample cell with approximately 25 cm^3 of instrument grade mercury. Record the mass of the mercury used to ±0.001 g, W_m.

8.2.11 Reinstall the sample cell containing the mercury onto the apparatus.

8.2.12 Re-evacuate the sample cell, manometer, and gas burette to a pressure below 1.35 mPa (10 nmHg).

8.2.13 Repeat 8.2.3-8.2.9.

8.3 *Buret Factor Calculations*:

8.3.1 For each set of data (see 8.2.9) determine the pressure change by measuring the difference in buret readings before and after helium dosing as follows:

$$P_{B1} = V_{B1} - V_{B2} \tag{1}$$

8.3.2 Determine the total buret pressure difference for each data set as follows:

$$P_{BT} = (V_{B1} - V_{B2})_1 + (V_{B1} - V_{B2})_2 + \ldots \tag{2}$$

8.3.3 Determine buret pressure to cell pressure ratio for each data set as follows:

$$A = \frac{P_{BT}}{P_c} \tag{3}$$

8.3.4 Determine the ratio of cell temperature to buret temperature for each data set as follows:

$$B = \frac{T_c}{T_B} \tag{4}$$

8.3.5 Determine the product of the temperature and pressure for each data set as follows:

$$C = A \times B \tag{5}$$

8.3.6 Determine the average C value for the empty sample cell (C_E) and the cell with the mercury (C_m).

8.3.7 Determine the volume of mercury used as follows:

$$V = W_m \div \text{density of mercury}$$

$$\text{density of mercury} = 13.5955\ \text{Mg/m}^3 \text{ at } 0°\text{C} \tag{6}$$

8.3.8 Determine the buret volume factor corrected to standard temperature and pressure (STP) as follows:

$$F_B = \frac{V}{C_E - C_m} \times \frac{273.15\ K}{101.32\ \text{kPa}} \tag{7}$$

9. Sample Preparation Procedure

9.1 Dry a portion of the standard reference black to be tested (such that the portion contains well in excess of 50 m^2 in surface area of the black) in a vacuum oven at 200°C and a pressure below 1.35 Pa (10 μmHg) for 1 h.

9.2 Weigh out a sample cell to the nearest 0.0001 g and record the mass.

9.3 Weigh into the cell a sample of the black to be tested, that has been dried as required in 9.1, so that the cell contains approximately 50 m^2 of surface area for the black.

9.3.1 If this is not a measurement of a standard reference

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[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

black, and the type of black is unknown, assume a surface area of 75 m ^{2}/g and weigh out approximately 0.5 g. Record the combined mass of the cell and black.

9.4 With apparatus at atmospheric pressure, seal the sample cell containing the carbon black onto the vacuum apparatus.

9.5 Turn on the mechanical vacuum pump. After pressure is reduced below 135 Pa (1 mmHg), proceed to 9.6.

9.6 Start up diffusion vacuum pump.

9.7 Place heating mantle around sample cell and de-gas the sample at 300 ± 10°C for 1 h or longer as required to obtain and hold a pressure less than 1.35 mPa (10 nmHg); record temperature and heating time. Periodically check the vacuum with the McCloud gage or similar instrument. A pressure less than 1.35 mPa (10 nmHg) should be maintained.

9.8 Remove heating mantle and allow the sample cell to cool to room temperature.

10. Calibration Procedure

NOTE 2—This procedure is designed to measure the dead volume (that is, helium factor) in the system using helium, as helium is not adsorbed onto the surface of the black at the temperature of liquid nitrogen.

10.1 When the sample has cooled, immerse the sample bulb to a depth of 10 cm in the liquid nitrogen contained in the Dewar flask.

NOTE 3—Since liquid nitrogen tends to evaporate rather rapidly, be sure to keep the level constant for the duration of the test.

10.2 Measure the helium factor of the sample cell system (that is, calibrate the system) using helium gas as follows:

10.2.1 Admit a dose of helium to the gas buret that is approximately 50 % of the volume of the buret.

10.2.2 Read and record gas buret volume (V_{B1}) and temperature (T_B).

10.2.3 Dose sample cell with approximately 2 cm^3 of helium. Read and record manometer pressure (P).

10.2.4 Read and record gas buret volume (V_{B2}), having dosed the sample with helium.

10.2.5 Repeat incremental dosing of sample cell with helium twice more; read and record buret volume, manometer pressure and buret temperature for each dosing.

10.2.6 Calculate helium factor in accordance with 12.2 in Section 12.

NOTE 4—When helium factors are calculated, the three results should not differ by more than ±4 μm^3/Pa (± 0.0005 cm^3/mmHg). If their differences are more than this, repeat 10.2.1-10.2.5 to obtain factors that are within 4 μm^3/Pa (0.0005 cm^3/mmHg) of each other.

10.3 While the cell is still immersed in liquid nitrogen, evacuate helium from the entire system. After approximately 15 min, read the vacuum with the McCloud or equivalent gage. When a pressure less than 1.35 mPa (10 nmHg) has been attained, begin measurement procedure.

11. Measurement Procedure

11.1 Fill the gas buret with nitrogen gas to approximately 75 % of its volume.

11.2 Dose the sample cell with an amount of nitrogen gas to give an approximate pressure reading of 4.7 kPa (35 mmHg). This value is just below the beginning of the linear region on the adsorption isotherm for carbon black. Read and record buret pressures (P_{B1}, P_{B2}), as done in 10.2, and temperature (T_B) along with the manometer pressure (P) for each dose.

11.3 Allow the pressure in the sample cell-manometer system to equilibrate for 0.5 h or more to obtain a constant pressure. Read and record manometer pressure (P).

11.4 For subsequent doses, introduce 1 to 1.5 cm ^{3} of nitrogen to the sample in successive doses. Obtain a minimum of five data sets in the pressure range of 6 kPa (45 mmHg) to 27 kPa (200 mmHg). In determining carbon black surface areas, it is not necessary to take readings at manometer pressures higher than 27 kPa (200 mmHg) since this value is beyond the linear region of the adsorption isotherm.

11.5 Obtain the saturation vapor pressure of liquid nitrogen (P_o) by accurately measuring the barometric pressure and adding 2 kPa (15 mmHg) to its value as follows:

$$P_o = \text{barometric pressure (kPa)} + 2\ \text{kPa} \quad (8)$$

NOTE 5—In principle, a more accurate means of measuring P_o is to immerse an identical, empty reference cell in a Dewar flask to a depth equivalent to the sample cell. Admit nitrogen gas into the reference cell to obtain equilibrium pressure (P_o), that is, approximately 103 kPa (775 mmHg).

11.6 With both vacuum pumps running, open the stopcocks so that the sample cell is open to the vacuum line. Remove the liquid nitrogen from around the sample cell, allowing adsorbed nitrogen to exhaust into the vacuum line.

11.7 Proceed to Section 12.

12. Calculation

12.1 *Sample Mass*:

$$\text{Mass of sample (dried)} = (\text{mass of cell} + \text{sample}) - (\text{mass of cell})$$
$$(\text{Record masses to } \pm 0.0001\ \text{g}) \quad (9)$$

12.2 *Helium Factor*— Calculate helium factor as follows:

$$\text{Helium factor} = \Sigma \frac{\left(\dfrac{\dfrac{V_B \times 273.15\ \text{K}}{101.32\ \text{kPa}} \times \dfrac{V_{B2} - V_{B1}}{T_B}}{P} \right)}{n} \quad (10)$$

where:

V_B = volume of buret (see Section 10),
T_B = temperature of buret in Kelvin (K = 273.15 + °C),
V_{B1} = initial volume in buret,
V_{B2} = final volume in buret,
P = pressure in manometer, and
n = number of data sets.

12.3 *Nitrogen Surface Area*:

12.3.1 Calculate volume of nitrogen admitted to the nearest± 0.0001 cm^3 as follows:

$$V_{ADM} = F_B \times \frac{P_{B2} - P_{B1}}{T_B} \quad (11)$$

where:

V_{ADM} = volume of gas admitted at stp,
F_B = buret factor,
P_{B2} = final pressure in buret (read after 0.5 h equilibration),
P_{B1} = initial pressure in buret (read before each dose), and

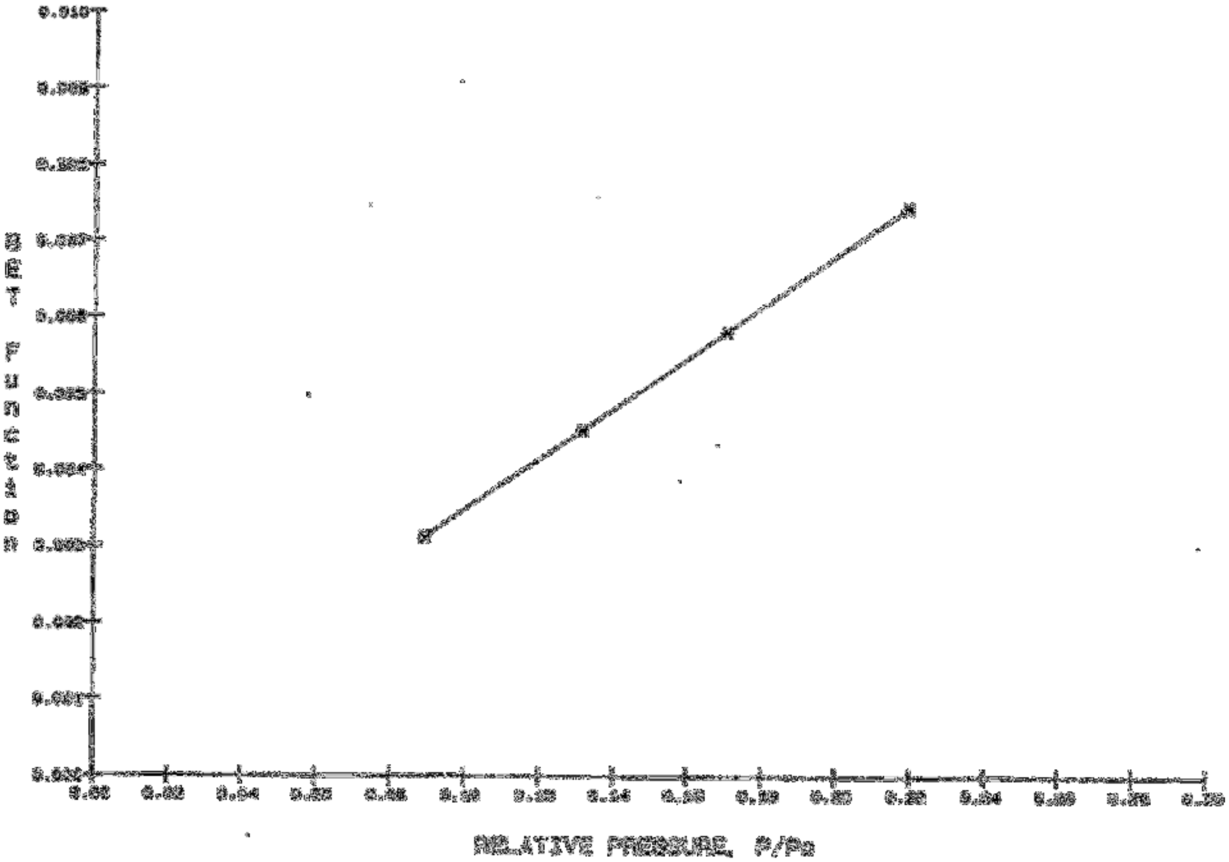

FIG. 2 B.E.T. Function Plot

T_B = buret temperature (temperature of insulating water jacket).

12.3.2 Calculate volume of nitrogen not adsorbed to the nearest ± 0.0001 cm^3 as follows:

$$V_{NA} = P \times \text{ helium factor} \times \text{gas law correction} \tag{12}$$

where:

V_{NA} = volume not adsorbed,
P = manometer pressure, and
gas law correction = (1 + deviation).

12.3.2.1 Deviation from the total gas law pressure is calculated as follows:

$$\text{Deviation in kPa} = (P)(5.148 \times 10^{-4}) \tag{13}$$

$$[\text{Deviation in mm Hg} = (P)(6.950 \times 10^{-5})] \tag{14}$$

12.3.3 Calculate volume of nitrogen adsorbed to the nearest 0.0001 cm^3 as follows:

$$V_{ADS} = V_{ADM} - V_{NA} \tag{15}$$

where:

V_{ADS} = volume of nitrogen adsorbed per gram of black in cm^3/g,
V_{ADM} = volume admitted at STP, and
V_{NA} = volume not adsorbed.

12.3.4 Calculate total volume of nitrogen adsorbed per gram of specimen to the nearest 0.0001 cm^3/g as follows:

$$V_{ADS/g} = \frac{V_{ADS} \text{ for each dosing in } cm^3/g}{\text{sample mass}} \tag{16}$$

where:

$V_{ADS/g}$ = total volume of nitrogen adsorbed per gram of black in cm^3/g.

12.3.5 Determine the surface area of the black using a B.E.T. plot from the Brunauer, Emmet, and Teller (B.E.T.)[4] equation as follows (see Fig. 2):

$$\frac{P}{V_{ADS/g}(P_o - P)} = \frac{1}{V_m c} + \frac{C - 1}{V_m c} \times \frac{P}{P_o} \tag{17}$$

12.3.5.1 Plot P/P_o on X-axis versus

$$\frac{P}{V_{ADS/g}(P_o - P)}$$

on Y-axis, for data sets having P/P_o in the range of 0.06 to 0.35 (typically the linear region of B.E.T. equation).

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[4] Brunauer, Emmet, and Teller, *Journal of American Chemistry Society*, Vol 60, 1938, p. 309.

where:

P = manometer pressure in kPa,

V = $V_{\mathrm{ADS/g}}$—total volume of nitrogen adsorbed per gram of black in cm^3/g,

P_o = saturation vapor pressure of nitrogen,

V_{M} = volume of nitrogen per gram that covers one monomolecular layer in cm^3/g,

C = a constant that is a function of average heat of adsorption of the monomolecular layer,

B = Y-axis intercept, ±0.00001,

M = slope of the straight line—determine slope to: ±0.00001, and

$V_M = \dfrac{1}{B+M}$

NOTE 6—Standard linear regression calculations can also be used to determine the slope and intercept of this function.

12.3.6 Calculate the nitrogen surface area to the nearest 0.1×10^3 m^2/kg (0.1 m^2/g) as follows:

$$\text{Surface area} = V_{\mathrm{m}} \times 4.35\ \mathrm{m^2/cm^3} \tag{18}$$

where:

4.35 = area occupied by 1 cm^3 of nitrogen = $\dfrac{(6.02 \times 10^{23})(16.2 \times 10^{-20})}{22\,400}$

6.02×10^{23} = Avogadro's number,

16.2×10^{-20} = area of nitrogen molecule in m^2, and

22 400 = number of cm^3 occupied by one mole of gas at STP.

NOTE 7—Commercial instruments are available for the measurement of nitrogen surface area by the multipoint B.E.T. Method. There are two alternatives to the classical procedure described above: the automated version of the vacuum apparatus described herein, and the continuous flow multipoint instruments.

Automated vacuum instruments will provide results equivalent to the procedure described above if careful calibration of the instrument, equivalent sample preparation, adherence to manufacturer's instructions for instrument operation, and equivalent data handling and calculations are performed.

Continuous flow instruments are used to generate multipoint nitrogen surface area data by using a number of gas mixtures of nitrogen in helium. Accurate knowledge of the gas compositions is essential. Nitrogen concentrations in the range of 7.5 to 20 % (volume percent) must be used to ensure that measurements will fall within the linear region of gas adsorption on carbon black. Strict adherence to manufacturer's instructions is required. Verification of the accuracy of such measurements by standardization to results obtained from vacuum type equipment is highly desirable.

TEST METHOD B—AUTOMATED NITROGEN SURFACE AREA BY THE STATIC VOLUMETRIC METHOD

13. Summary of Test Method

13.1 A carbon black sample is placed in a known volume cell and evacuated to less than 5 millitorr of vacuum. Using the ideal gas equation, the volume of nitrogen required to give a predetermined relative pressure is calculated and dosed into the sample cell. Any additional nitrogen required to attain this relative pressure is due to adsorption by the carbon black. Based on the volume of nitrogen adsorbed at various relative pressures, the surface area is calculated.

14. Theory of Test Method

14.1 The determination of surface area from the B.E.T. theory is a straightforward application of the B.E.T. equation:

$$\frac{1}{V[(P_o/P)-1]} = \frac{1}{V_M C} + \frac{C-1}{V_M C} \times \frac{P}{P_o} \tag{19}$$

where:

V = volume of nitrogen adsorbed, cm^3,

P = pressure, kPa,

P_o = saturation vapor pressure of nitrogen, kPa,

V_M = volume of nitrogen that covers one monomolecular layer, cm^3, and

C = B.E.T. constant.

14.2 A plot of

$$\frac{1}{V[(P_o/P)-1]}$$

versus P/P_o will usually yield a straight line in the range 0.05 to 0.35. Solving the B.E.T. equation for V_M gives:

$$V_{\mathrm{M}} = \frac{1}{M+B} \tag{20}$$

where:

M = slope of straight line, and

B = y-intercept.

15. Apparatus

15.1 *Automated Nitrogen Surface Area Analyzer*, to include vacuum system, Dewar flasks, and data analysis system.

15.2 *Degassing Station*, to include vacuum system and heating mantles capable of maintaining 300 ± 10°C.

15.3 *Balance*, analytical, with 0.1 mg sensitivity.

15.4 *Sample Cells*, which, when attached to the vacuum system, will maintain a pressure below 0.7 Pa (5 µm Hg).

16. Reagents

16.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

16.2 *Liquid Nitrogen*.

16.3 Ultra high purity nitrogen gas cylinder, or other source of prepurified nitrogen gas.

16.4 Ultra high purity helium gas cylinder, or other source of prepurified helium gas.

17. Sample Preparation

17.1 Place a clean sample tube on the degassing station and heat at 300°C for 0.5 h at a pressure below 2.7 Pa (20 µm Hg).

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[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

The insertion of a glass rod into the sample tube stem will reduce the void volume of the stem, thus improving testing precision.

17.2 Cool the sample tube to room temperature, then backfill, preferably with helium to atmospheric pressure. Place a stopper on the sample tube and weigh it to the nearest 0.0001 g and record as mass *A*.

17.3 For samples of unknown surface area, place approximately 0.2 g of carbon black in the sample tube. For known surface area levels, use an amount of carbon black that is equivalent to 20 to 50 m^2 of surface area. Clean the sample tube stem with a pipe cleaner.

17.4 Place the sample tube containing the carbon black on the degassing station and open the vacuum valve.

17.5 Place the heating mantle on the sample cell and heat at 300°C for 1 h or longer to obtain and hold a pressure less than 2.7 Pa (20 μm Hg).

17.6 Remove the heating mantle and allow the sample cell to cool to room temperature. Backfill the sample tube with helium to atmospheric pressure, remove from the degassing station, and close it with a stopper.

18. Sample Analysis

18.1 Place the sample tube containing the carbon black on the nitrogen surface area analyzer.

18.2 Initial the experiment. The following experimental steps, necessary to attain accurate results, can be automatically determined by most automated nitrogen surface area analyzers.

18.2.1 *Leak Test*—The vacuum volumetric technique relies on precise pressure measurements to determine the surface area of carbon black. Any leaks in the system will result in erroneous surface area measurements. A minimum of a 2 min leak test of the sample and P_o cells is required. Any significant pressure change in the cells over this time interval will result in the abortion of the experiment.

18.2.2 *Transducer Linearization*—If separate sample and transducer manifolds are utilized by the testing equipment, it is necessary to zero and linearize the transducers prior to each experiment.

18.2.3 *Sample Cell Volume*—In determining the void volume of the sample cell, both the warm zone and cold zone (section submersed in liquid nitrogen) must be measured prior to each analysis. Non-ideality gas corrections are applied to the volume of gas in the cold zone.

18.2.4 *Saturated Vapor Pressure (P_o)*—The saturated vapor pressure of nitrogen is affected by the purity of the liquid nitrogen and ambient pressure. Dissolved impurities in the liquid N_2 will usually cause the bath temperature to increase sufficiently to cause a 1.4 to 2.7 kPa (10 to 20 mm Hg) increase in theoretical vapor pressure. Often, P_o is assumed to be 103 kPa (775 mm Hg); however, for maximum accuracy the actual P_o should be measured.

18.3 Once the above conditions are measured, volumes of pure nitrogen are calculated, measured, and dosed into the sample cell. This process is repeated until equilibrium conditions are satisfied at the desired relative pressure. The summation of the dose volumes required to reach a particular relative pressure constitute the adsorption volume data at the various relative pressures. The adsorption volumes are measured at relative pressures of 0.05 to 0.30. A minimum of 5 relative pressures are recommended.

18.4 Backfill the sample tube at ambient temperature with the atmosphere used in 17.2. Remove the sample tube from the instrument, stopper it, and weigh it to the nearest 0.0001 g and record as mass *B*.

18.5 Nitrogen adsorbed by the carbon black at the various relative pressures is used to prepare the B.E.T. plot. The data points that give the best straight line are used to calculate the slope and *y*-intercept. The slope and *y*-intercept are used to calculate the surface area. For examples of how to select the proper relative pressure range, see Table 1.

18.6 A B.E.T. plot that yields a negative *y*-intercept could be indicative of the presence of micropores (<3 nm diameter), but other factors can produce a negative *y*-intercept. The surface area is calculated from the pressure range that yields the highest correlation coefficient and a positive *y*-intercept. A minimum of three partial pressure points must be used for the relative pressure range to measure the correlation coefficient.

19. Calculation

19.1 Calculate the sample mass as follows:

TABLE 1 Example of Multipoint B.E.T. NSA Data Analysis

N121[A]

P/Po	Vol. Ads. dm^3/kg (cm^3/g)	Approx. Rel. Pressure Range	Correlation Coefficient	NSA (m^2/g)
0.0523	27.416	...	...	...
0.1057	30.453	...	...	...
0.1574	33.013	0.05–0.15	0.999974	124.7
0.2086	35.392	0.05–0.20	0.999988	124.5
0.2593	37.810	0.05–0.25	0.999975	124.1
0.3078	40.341	0.05–0.30	0.999897	123.2

N326[B]

P/Po	Vol. Ads. dm^3/kg (cm^3/g)	Approx. Rel. Pressure Range	Correlation Coefficient	NSA (m^2/g)
0.0613	16.975	...	...	...
0.1122	18.618	...	...	...
0.1619	20.159	0.05–0.15	0.999938	75.8
0.2117	21.726	0.05–0.20	0.999933	76.3
0.2608	23.335	0.05–0.25	0.999957	76.5
0.3104	25.051	0.05–0.30	0.999972	75.4

N683[C]

P/Po	Vol. Ads. dm^3/kg (cm^3/g)	Approx. Rel. Pressure Range	Correlation Coefficient	NSA (m^2/g)
0.0524	8.294	...	...	...
0.1029	9.213	...	...	...
0.1558	10.045	0.05–0.15	0.999957	38.2
0.2069	10.839	0.05–0.20	0.999961	38.4
0.2568	11.643	0.05–0.25	0.999978	38.4
0.3065	12.464	0.05–0.30	0.999960	38.3

[A] The best[D] surface area is measured between 0.05 and 0.20 relative pressure.
[B] The best surface area is measured between 0.05 and 0.30 relative pressure.
[C] The best surface area is measured between 0.05 and 0.25 relative pressure.
[D] The term "best" is defined as the highest correlation coefficient.

$$S = B - A \tag{21}$$

where:

S = sample mass, g,
A = mass of sample tube, stem, and stopper, and
B = mass of sample tube, stem, stopper, and sample after analysis.

19.2 Calculate the nitrogen surface area (NSA) to the nearest 0.1×10^3 m^2/kg (0.1 m^2/g) as follows:

$$\mathrm{NSA} = \frac{V_m N A_{cs}}{22\,400 \times S} \tag{22}$$

where:

N = Avagadro's Number, 6.023×10^{23} molecules/mole,
A_{cs} = Cross-sectional area of nitrogen molecule, 16.2×10^{-20} m^2/molecule, and
22 400 = number of cm^3 occupied by one mole of gas at STP.

20. Report

20.1 Report the following information:

20.1.1 Proper sample identification.

20.1.2 Method used, A or B.

20.1.3 Number of data points and relative pressures used to obtain the results.

20.1.4 The sample mass to the nearest 0.1 mg.

20.1.5 Result obtained from an individual determination, reported to the nearest 0.1×10^3 m^2/kg.

21. Precision and Bias

21.1 These precision statements have been prepared in accordance with Practice D 4483. Refer to this practice for terminology and other statistical details.

21.2 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials used in the particular interlaboratory program described below. The precision parameters should not be used for acceptance or rejection testing of any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols of the test method. Any appropriate value may be used from Table 2

21.3 A type 1 inter-laboratory precision program was conducted as detailed in Table 3. Both repeatability and reproducibility represent short term (daily) testing conditions. The testing was performed using two operators in each laboratory performing the test once on each of two days (total of four tests). A test result is the value obtained from a single determination. Acceptable difference values were not measured. The between operator component of variation is included in the calculated values for r and R.

TABLE 2 Precision Parameters for D 4820 Surface Area by Multipoint B.E.T. Nitrogen Absorption, (Type 1 Precision)

Units	10^{-5} m^3/kg (cm^3/100 g)				
Material	Mean Level	Sr	(r)	SR	(R)
N762	64.75	0.36	1.6	0.93	4.1
IRB#6 (N330)	99.63	0.36	1.0	0.63	1.8
N650	120.89	0.58	1.3	2.03	4.8
N550	121.01	0.57	1.3	1.92	4.5
N234	123.94	0.49	1.1	1.07	2.4
SRB A5 (N135)	136.69	0.44	0.9	0.94	1.9
Average	111.15				
Pooled Values		0.47	1.2	1.36	3.5

TABLE 3 Interlaboratory Precision Program

Nominal Test Period	Material	Number of Laboratories
September 1995	N234	35
March 1996	N650	50
October 1996	IRB#6 (N330)	45
March 1997	N762	53
September 1997	SRB A5 (N135)	45
March 1998	N550	46

21.4 The results of the precision calculations for this test are given in Table 2. The materials are arranged in ascending" mean level" order.

21.5 *Repeatability*—The pooled relative repeatability, (r), of this test has been established as 1.5 %. Any other value in Table 2 may be used as an estimate of repeatability, as appropriate. The difference between two single test results (or determinations) found on identical test material under the repeatability conditions prescribed for this test will exceed the repeatability on an average of not more than once in 20 cases in the normal and correct operation of the method. Two single test results that differ by more than the appropriate value from Table 2 must be suspected of being from different populations and some appropriate action taken.

NOTE 8—Appropriate action may be an investigation of the test method procedure or apparatus for faulty operation or the declaration of a significant difference in the two materials, samples, etc., which generated the two test results.

21.6 *Reproducibility*—The pooled relative reproducibility, (R), of this test has been established as 3.1 %. Any other value in Table 2 may be used as an estimate of reproducibility, as appropriate. The difference between two single and independent test results found by two operators working under the prescribed reproducibility conditions in different laboratories on identical test material will exceed the reproducibility on an average of not more than once in 20 cases in the normal and correct operation of the method. Two single test results produced in different laboratories that differ by more than the appropriate value from Table 2 must be suspected of being from different populations and some appropriate investigative or technical/commercial action taken.

21.7 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (true) test property value. Reference values do not exist for this test method since the value or level of the test property is exclusively defined by the test method. Bias, therefore, cannot be determined.

22. Keywords

22.1 B.E.T.; Brunauer/Emmet/Teller; carbon black; nitrogen adsorption; nitrogen surface area; surface area by multipoint B.E.T. method

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