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**Removal of Boron and Strontium from Seawater by
Activated Carbon Produced from Olives Crushed Seeds**

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Thesis submitted to the Institute of Water and Environment (IWE),
In partial fulfillment of the requirements for the degree of
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Removal of Boron and Strontium from Seawater by Activated Carbon Produced from Olives Crushed Seeds

إزالة البورون والاسترانشيوم من مياه البحر بالكربون المنشط المصنع من نوى
الزيتون المطحون

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DEDICATION

My greatest thanks are to my lovely parents and family for their understanding, patience, and continuous support during my study which provided me the suitable environment to achieve this goal.

I wish to thank my wife for her patience, as her always remained very close, loving and supporting me, sharing both the failure and the joys of success. Thus, I would like to dedicate this thesis to the soul of my beloved mother, to my cherished father, and my brothers and sisters to whom I owe everything since I was born.

*This thesis is kindly dedicated to my lovely wife
and daughters, Noor, Malak and Mariam, who
showered me with their support and encouragement
me at all stages of my study.*

To my friends who supported and helped me a lot.

Finally, this thesis is dedicated to all those who live and work for

Palestine...

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ABSTRACT.

The Gaza strip suffers from the shortage of water resources and the leakage of seawater into the underground water tanks which has a negative impact upon increasing the concentration of boron and strontium in underground water. Another reason behind the high concentration boron in underground water is using agricultural fertilizers. These negative impact pose an economic burden upon the country through the process of pollutants removal.

Boron and strontium are two of the most existing elements in sea water, and it is hard to remove them through the elementary stages of desalination processes. This will lead to using a more advanced system in the desalination process which pose an economic burden upon the country through the process of pollutants removal.

This study aims at participating in the process of boron and strontium removal through an economical and practical method using activated carbon produced from crushed olive seeds (olive pressing waste). For this purpose, several laboratory experiments have been conducted using activated carbon in the process of boron and strontium adsorption.

Through this study, crushed olive seeds have been carbonized in a temperature of 500-550 °C at inert environment by flowing Nitrogen 300-500 cm³ per minute. It was then activated using heat and potassium hydroxide. Plenty of factors have been tested to figure out the efficiency of activated carbon under the influence of different factors such as time, pH, temperature, and the amount of the carbon used.

The results showed the efficiency of activated carbon through the previously mentioned factors. The more activated carbon we used, the better efficiency the adsorption becomes. The best pH of the adsorption process was between 6.5 – 7.5. The temperature has a negative impact of the efficiency of the adsorption process. The higher the temperature is, the less the adsorption becomes.

Samples of already known concentration of boron and strontium have been used adding the produced activated carbon. The findings showed the efficiency of the product in removing boron at the rate of 85% and strontium at the rate of 55%. Representative seawater samples have been used to check the efficiency of the produced activated carbon in the removal process. The results showed

that it removed around 3.7% of boron and 2.8% of strontium. Initial and final concentrations of metal were measured using Inductively Coupled Plasma (ICP).

Consequently, this study explains the feasibility of using activated carbon produced from crushed olive seeds in the removal process of boron and strontium. This product can be considered a competitive economical product since it has a great significance regarding the disposal of agricultural waste as well as decreasing the economic burden of the removal of boron and strontium.

الملخص العربي

يعاني قطاع غزة من شح الموارد المائية وتداخل مياه البحر إلي الخزان الجوفي مما له اثر سلبي على زيادة البورون والاسترانشيوم في المياه الجوفية. هناك عوامل اخرى تؤثر على زيادة البورون في المياه الجوفية منها سوء استخدام المبيدات الزراعية. وهذه التأثيرات السلبية لها عبء اقتصادي في عملية إزالة هذه الملوثات.

يعتبر البورون والاسترانشيوم من العناصر المتواجدة في مياه البحر ويصعب إزالتها والتخلص منها بالمراحل الابتدائية الخاصة بعمليات تحلية مياه البحر مما يتطلب استخدام نظام متقدم في عملية التحلية ولما له من عبئ اقتصادي في عملية إزالة هذه الملوثات.

تهدف هذه الدراسة إلى المساهمة في عملية إزالة البورون والاسترانشيوم بطريقة اقتصادية وعملية بواسطة الكربون المنشط المنتج من نوى الزيتون المطحون (مخلفات عصر الزيتون) .

ولتحقيق هذا الهدف تم القيام بالعديد من التجارب المخبرية باستخدام الكربون المنشط في عملية امتزاز البورون والاسترانشيوم.

من خلال هذه الدراسة أجريت عملية تفحيم نوى الزيتون في درجة حرارة 500 – 550 درجة مئوية وبوجود غاز النيتروجين الخامل بمعدل سريان 300 – 500 سم³/دقيقه. ومن ثم تنشيطه باستخدام هيدروكسيد البوتاسيوم والحرارة.

ثم إجراء العديد من العوامل لمعرفة كفاءة الكربون المنشط تحت تأثير عوامل مختلفة مثل الزمن والرقم الهيدروجيني ودرجة الحرارة وكمية الكربون المستخدم.

أظهرت النتائج كفاءة الكربون المنشط من خلال العوامل السابقة حيث كلما زادت كمية الكربون المنشط زادت كفاءة الامتزاز. أفضل رقم هيدروجيني لعملية الامتزاز ما بين 6.5 – 7.5. درجة الحرارة لها تأثير سلبي على كفاءة الامتزاز فكلما زادت الحرارة قل معدل الامتزاز .

استخدمت عينات معلومة التركيز للبورون والاسترانشيوم وتم إضافة الكربون المنشط المنتج وأظهرت النتائج بمدى كفاءة هذا المنتج في إزالة البورون حوالي 85 % بينما الاسترانشيوم 55 %. تمت عملية فحص البورون والاسترانشيوم والمحاليل الخاصة بهذه العناصر باستخدام جهاز فحص المعادن الثقيلة (المقياس البلازمي الحثي) ICP.

استخدم عينات ممثلة لمياه البحر وفحص مدى كفاءة الكربون المنتج في عمليه إزالة هذه الملوثات وأظهرت بإزالة حوالي 3.7% من البورون 2.8% من الاسترانشيوم.

فيتضح من خلال هذه الدراسة بجدوى استخدام الكربون المنتج من نوى الزيتون في إزالة البورون والاسترانشيوم ويمكن اعتباره منافسا تجاريا ولما له من مميزات هامة في اعاده استخدام المخلفات الزراعية والتقليل من العبء الاقتصادي في عمليه إزالة البورون والاسترانشيوم.

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LIST OF ABBREVIATIONS

Abbreviation	Name
°C	Celsius
AC	Activated Carbon
PWA	Palestinian Water Authority
cm ³ /min	Cubic Centimeter per minute
CMWU	Coastal Municipalities Water Utility
FAO	Food and Agricultural Organization
g	Grams
H	Hours
RO	Reverse Osmosis
MCM	Million Cubic Meter
WHO	World Health Organization
B	Boron
Sr	Strontium
EPA	Environmental Protection Agency
OCS	olives crushed seeds
ICSCs	International Chemical Safety Cards
ppm	parts-per-million
IPCS	International Programme on Chemical Safety
GAC	Granular Activated Carbon
PAC	Powdered activated carbon
EAC	Extruded activated carbon
N ₂	Nitrogen
ICP-OES	Inductively coupled plasma optical emission spectrometry
MOA	Ministry Of Agriculture
mm	Millimeter
ml	Milliliter
mg/L	Milligram per Liter
m ³	Cubic meter
N	Normality
pH	Hydrogen Power
UNEP	United Nations Environment Program
Mm ³ / yr	Million Cubic Meter per year
EU	European Union
TDS	Total Dissolved Solid
Eh	Redox Potential

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CHAPTER ONE

INTRODUCTION

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Gaza Strip is one of the semi-arid areas where rainfall is falling in the winter season from September to April; the rate of rainfall is varying in the Gaza Strip and ranges between 200mm/year in the south to about 400mm/year in the north (PWA, 2018). Groundwater aquifer is considered the main and only water supply source for all kind of human usage in the Gaza Strip. This source has faced a deterioration in both quality and quantity for many reasons such as low rainfall, increased urban areas which led to a decrease in the recharge quantity of the aquifer as well as the increasing population which will deplete the groundwater aquifer and lead to seawater intrusion in some areas. The average yearly abstraction from the groundwater reached more than 200M m³, where the recharge to the groundwater from all different components reached about 110M m³(PWA, 2018).

Gaza Strip is one of the highest population intensity areas in the world where the population has reached more than 1.6 million inhabitants, with an annual growth rate of 3.3% (GETAP, 2011) living within 378Km² (UNEP, 2003). Gaza Strip is facing a serious shortage of fresh water supply to the living people both in quantity and bad quality due to pollutants which entered the groundwater. Groundwater shortage is being accumulated over the years, where PWA states that there's a yearly shortage of around 50 to 60 million cubic meter (MCM). These accumulations of deficits over the years create low pressure zone in the groundwater which force seawater to intrude the groundwater to substitute the groundwater deficit. This leads to seawater intrusion in many areas along the Gaza Coastal Beach. Seawater intrusion reaches more than 3km inland as shown in PWA and CMWU maps for chloride concentration distribution. Figure (1.1.) shows Chloride distribution over years:

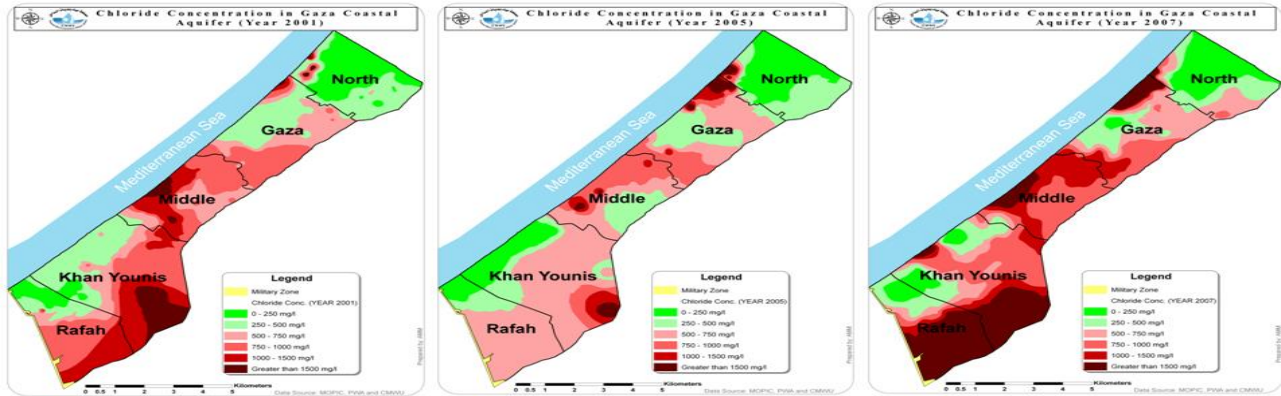


Figure 1.1: Chloride distribution over years (Mushtaha, 2008)

More than 5000 wells are distributed all over the Gaza Strip (200 for domestic usage and the rest for the agricultural). Due to heavily abstraction from the aquifer, the groundwater became polluted by high chloride content due to seawater intrusion. Figure (1.2.) shows agricultural and illegal Water well Location; figure (1.3) shows domestic water well locations.

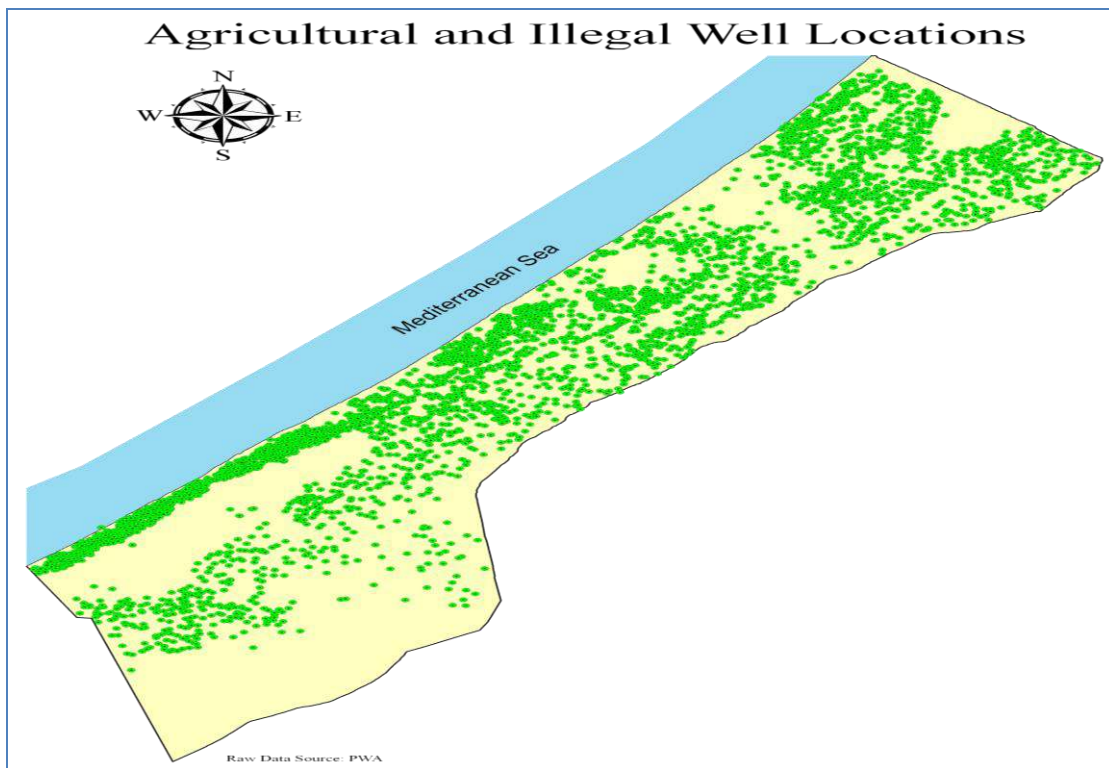
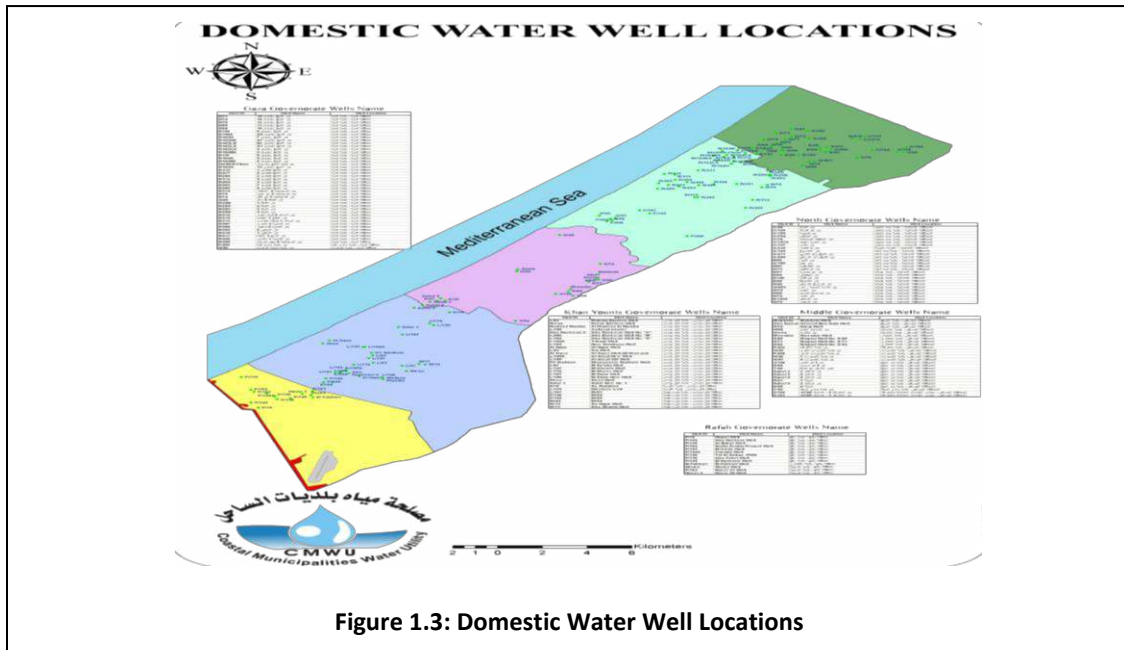


Figure 1.2: Agricultural and Illegal Well Locations



A strategic plan was set for new water resource to the supply with fresh water to the Gaza Strip people. This new water resource is translated to be sea water desalination plant on large and small scale units. One of sea water problems is the existence of boron and strontium. Boron and strontium are generally distributed in the environment, occurring naturally or due to anthropogenic contamination (Simonnot, et al., 2000). Though boron and strontium are essential micronutrient for plants and animals including humans as well, the line between deficiency and excess is narrow and excessive amount of boron and strontium could have negative effect on health. The regulation for boron and strontium in drinking water varies greatly from country to another (WHO-EU drinking water_1998).

Recently, boron and strontium have been classified by the European Union as a pollutant of drinking water in national and international drinking water directives. Moreover, boron has increasingly become a concern in recent years due to its adverse effects on agriculture at concentration as low as 1 mg/L for sensitive crops such as citrus and avocado and between 1-4 mg/L for tolerant crops like onion and carrots. The recommended values according FAO irrigation water standard are between 0.5-15 mg/l depending on the type of agricultural crops (Ayers, et al , 1985) .

There have been no bad effects of strontium on human health, but some studies proved that it affects the human health causing lung cancer, for example. It may also cause anemia and oxygen shortages, and at extremely high concentrations it is even known to cause cancer as a result of

damage to the genetic materials in cells. Moreover, when strontium uptake is extremely high, it can cause disruption of bone development.(ATSDR ,2004).

Studies showed that Boron affects human health badly. The most common central nervous system findings were oedema and congestion of the brain and meninges. Other common findings included liver enlargement, vascular congestion, fatty changes, swelling, and granular degeneration and brain tumour- arthritis. (ATSDR, 2010)

In the last years, many Mediterranean countries that mainly depend on the Reverse Osmosis RO technologies to desalinate water and reusing the treated wastewater for irrigation purposes have been suffering from high boron and strontium concentrations in the permeate water. Whereas conventional water and wastewater treatment technologies like slow sand, rapid sand, coagulation and sedimentation are surrendered in front of a small size. Even the advanced techniques of water treatment such as electro-dialysis and common RO membrane cannot remove boron and strontium to the level needed for drinking or irrigation.

Many special technologies can reduce the boron and strontium content from the desalinated water. Boron and strontium selective resins can remove boron efficiently; almost 100% from seawater reverse osmosis. However, the quantity of chemicals required for regeneration is large and disposal could be a problem. Moreover, it is not economical for high levels of boron and strontium due to expensive regeneration process (Magara et al,1998 : Redondo et al, 2003) .

There have been many studies that tackled the removal of heavy metals. for the removal process, Ion exchange, reverse osmosis, and chemical precipitation have been investigated. The problem is that they were very expensive. Adsorption has been proved to be a potentially feasible alternative. However, using activated carbon has been proved to be the feasible alternative for adsorption. Using activated carbon can also be expensive especially if proper raw materials are not available. If so, we should import carbon.

Many locally generated agricultural wastes have been tested in the production of activated carbon in the developing countries. Examples of these wastes are cotton stalk, rice straw, sugar cane bagasse, and others which, according to previous studies, are available at low cost and contain high carbon content, and may be effective in the removal of heavy metals.

1.2 Problem Statement

As stated earlier, sea water desalination plants will be the main fresh water supply to more than 1.8 million inhabitants in the Gaza strip and based on and based to manage this source along with the groundwater must be provided up 55 million cubic meter to substitute the current groundwater.

These additional quantities of freshwater will enhance the long term water sustainability in the Gaza Strip, but one of the new challenges accompany with the sea water desalination plants will be the pollutants originated from the sea as the boron and strontium (EPA). The average concentration of strontium in sea water is approximately 8 mg/L (Demayo 1986). In groundwater, the average concentration of strontium is <0.5 mg/L (ATSDR, 2004). High levels of boron are found in seawater (4.6mg/l), domestic wastewater (0.5- 2mg/l), and regional groundwater, for example Italy, Cyprus and Greece have boron content up to 8 mg/l) (Polat,et.al., 2004).

From the recent survey carried out by CMWU indicate a high concentration of those two pollutants in the Groundwater especially in wells that are very close to the sea. The consultant interpretation of the results stated that those two main pollutants refer to the sea water. Knowing that the sea water desalination plant stages are divided into two stages (for desalinating the sea water). The first stage of sea water desalination is to remove the chemical parameters from the source (sea water) and the second stage is to remove the heavy metals including the boron and strontium and other pollutants parameter (Taniguchi, et.al, 2010).

1.3 Research Aim

To study the potential of removing of the boron and strontium from the seawater by using activated carbon produced from olives crushed seeds.

1.4 Research Objective

The main objective of this research is to show the possibility of removal of the boron and strontium by activated carbon produced from olives crushed seeds. This will evaluate the capacity of the activated carbon produced from olives crushed seeds on removing the strontium and boron from the seawater as a pre-treatment process for the RO-Plants, which will help in completing the desalination of the sea water without passing to the second pass of membranes.

1.5 Research Importance

The importance of this study has a number of dimensions. The first dimension is lessening the cost of water produced from sea water desalination. The second dimension of this study is improving water quality, to match the required standards for reusing it in irrigation and drinking. The third dimension is to decrease organic pollutant from the environment and convert it to a product can make use of them without causing damage to the environment such as converting olives crushed seeds to activated carbon.

1.6 Research Methodology

The steps for this research work are divided in more than seven phase:

Stage 1: Preparation activated carbon from olives crushed seeds.

Stage 2: Determination concentration of strontium and boron in sea water.

Stage3: Experiments will be performed to find out the efficiency of removing these strontium and boron by the activated carbon produced by OCS.

Stage 4: Effect of pH in the removal strontium and boron.

Stage 5: Effect of Time in the removal strontium and boron.

Stage 6: Effect of Temperature in the removal strontium -and boron .

Stage 7: Data analysis, thesis writing and conclusions and recommendations.

CHAPTER TWO
LITERATURE REVIEW

CHAPTER TWO

LITERATURE REVIEW

2.1 Water production

The aquifer of the Gaza strip is overexploited, where more than 60 MCM is the yearly deficit of groundwater. The average yearly abstraction reached more than 170 MCM (PWA, 2018), where the recharge to the groundwater from all components reached 110 MCM. This condition is due to high population increase, leading to increasing water demand. Because higher water demands compared the sustainability of existing available groundwater, which is the main water source of water uses in the Gaza Strip. To overcome the water problem in the Gaza Strip (both quantity and quality), PWA policy and strategy is finding new water sources for drinking. For water resources management, additional water source in the Strip is desalinated seawater.

2.2 Boron

Boron is semimetal, situated in Block P (group 13) of the periodic table. In its own properties it is located somewhere between aluminum and carbon. The stable isotopes of boron are of mass 10 and 11 with estimated 20:80% ratio (K.L. Tu et. al., 2011). Elemental boron has a high melting point, good hardness and is a rather poor conductor of electricity. Boron is a chemical element with atomic number of 5 and the boron has various oxidation states compounds but the most significant and common is +3. It appears in lower oxidation states +1, 0 or less than 0, but these states are found in compounds such as e.g. higher borates only (P.P. Power et. al., 2010).

2.2.1 Boron in the environment

Boron is widely distributed in the environment, occurring naturally or from anthropogenic contamination, mainly under the form of boric acid or borate salts. Boron is found in the earth's crust at an average concentration of about 10 mg/L. Boron is actually a mixture of two stable isotopes, ^{10}B (19.8%) and ^{11}B (80.2%) (WHO, 1998). The most important commercial borate products and minerals are borax pentahydrate, borax, sodium perborate, boric acid, colemanite and ulexite. The production of boron compounds has increased in recent years, due to increasing demands for these compounds in nuclear technology and production of insulation and textile grade fiber, borosilicate glass, heat-resistant materials, catalysts, enamels, glazes and agricultural products (Simonnot et. al., 2000; Okay et.al, 1985; Şener et.al, 1988; Şahin et al , 2002; Badruk et. al., 1999).

Boron is essential element for the cultivation of fruits and vegetables. However, if it is present in amounts larger than required, it becomes toxic (Nadav, 1999). It also affects the environment due to the use of borates and perborates in the home and in industry, by escaping from treated wood or paper, sewage and sewage sludge disposal (WHO, 2003), (Ahmed et al, 2010). In the case of a seawater source the typical boron concentration in the raw water is 4.5 mg/L (Ahmed et al, 2010), (Keren et al, 1982).

Boron enters the environment mainly from the weathering of boron-containing rocks, from seawater in the form of boric acid vapour and from volcanic and other geothermal activity such as geothermal steam (Al-saifi, 2011) (Culver et al., 2001). Borates in detergents, soaps, and personal care products can also contribute to the presence of boron in the environment (ATSDR, 1992). Some surface waters contain boron as boric acid. For instance, boron more than 10 mg/L frequently occurs in hot spring waters. In addition, industrial wastewaters also contain boron at unacceptable concentrations (Jyo et al., 2001). Table 1 shows boron-containing minerals of commercial importance.

Table 1: Boron- containing minerals of commercial importance

Mineral	Chemical Composition	% Boron
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11}\cdot 5\text{H}_2\text{O}$	15.78
Datolite	$\text{CaBSiO}_4 \cdot \text{OH}$	6.76
Hydroboracite	$\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$	15.69
Kernite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$	14.90
Priceite	$\text{Ca}_4\text{B}_{10}\text{O}_{19} \cdot 7\text{H}_2\text{O}$	15.48
Proberite	$\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$	15.39
Sassolite	H_3BO_3	17.48
Szaibelyite	$\text{MgBO}_2 \cdot \text{OH}$	12.85
Tincal (borax)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	11.34
Tincalconite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	15.16
Ulexite	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$	13.34

2.2.2 Boron in seawater

According to Mellor (1980), Boron comes in the tenth rank of the most abundant elements in oceanic salts. It varies in concentration in the Mediterranean Sea. However, The global average is

between 4.6-4.8 mg/ L as stated by Argust (1998). Anderson et al. (1994) state that Boron can be transferred from sea water to the atmosphere through injecting boron salts into the atmosphere directly at the water-in inference and through the volatilization of boron as boric acid, H_3BO_3 . According to Argust (1998); Romheld and Marschner (1991), each year between 1.3 and 1.4 million tons of boron are transmitted to the atmosphere from marine sources through these devices.

Argust(1998) suggested that boron may be available in other reservoirs in the hydrologic cycle such as groundwater, surface water and ice. According to Argust (1998), boron concentration varies from 0.017 mg/l to 1.9 mg/l in most ground water because of several parameters such as the proximity to sea, geothermal activity, presence of boron-rich minerals, etc.

2.3 Strontium (Sr)

Strontium is the chemical element with the symbol Sr and atomic number 38. An alkaline earth metal, strontium is a soft silver-white yellowish metallic element that is highly chemically reactive. The metal forms a dark oxide layer when it is exposed to air. Strontium has physical and chemical properties similar to those of its two vertical neighbors in the periodic table, calcium and barium. It occurs naturally mainly in the minerals celestine and strontianite, and is mostly mined from these. Strontium can exist in two oxidation states: 0 and +2. Under normal environmental conditions, only the +2 oxidation state is stable enough to be important. strontium is usually found in nature in the form of minerals.

2.3.1 Strontium in the environment

Strontium can be released into the air (mainly as strontium oxide) by natural processes (e.g. weathering of rocks, wind re suspension and sea spray) or as a result of human activities (e.g. milling, processing, coal burning and phosphate fertilizer use). In air, the oxide rapidly forms the hydroxide or carbonate. Atmospheric strontium is returned to the ground by deposition. Strontium is released to surface water and groundwater by natural weathering of rocks and soils. Plants readily absorb strontium (ICSCs) International Chemical Safety Cards.

It is found in igneous rocks at 375ppm; shale at 300ppm; sandstone at 20ppm; limestone at 610ppm; fresh water at 0.08ppm; sea water at 8.1ppm; soils at 300ppm. Strontium 90, the man-made product, does not occur in nature Strontium is a metallic element, in the same chemical family as calcium and magnesium. Natural strontium is not radioactive and exists in four stable isotopic forms: ^{88}Sr (82.6%), ^{86}Sr (9.9%), ^{87}Sr (7.0%) and ^{84}Sr (0.6%). Strontium accounts for 0.02–0.03%

of Earth's crust, where it is found mainly as celestite (strontium sulfate) or strontianite (strontium carbonate) (IPCS). Most importantly, ⁸⁹Sr and ⁹⁰Sr are formed during nuclear reactor operations and nuclear explosions (ATSDR, 2004) . Details of the chemical identification of strontium compounds are clear in table (2).

The biological behavior of strontium resembles that of calcium. Strontium occurs in high-calcium foods like milk and milk products. It is stored in bones and teeth .Strontium reacts with water slowly, generally to strontium hydroxide and hydrogen gas. It reacts with water quicker than calcium, slower than barium.

The following reaction mechanism is applicable:

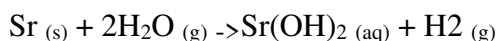


Table 2: Chemical identification of strontium and strontium compounds (Adapted from ATSDR, 2004)

Chemicalname	Synonyms	Chemical formula	Relative M. wt
Strontium	—	Sr	87.6
Strontiumacetate	Strontiumdiacetate	$\text{Sr}(\text{O}_2\text{CCH}_3)_2$	205.7
Strontiumcarbonate	Carbonicacid, strontiumsalt(1:1); strontianite	SrCO_3	147.6
Strontiumchloride	Strontiumdichloride	SrCl_2	158.5
Strontiumchromate	Chromicacid, strontiumsalt	SrCrO_4	203.6
Strontiumfluoride	Strontiumdifluoride	SrF_2	125.6
Strontiumhydroxide	Strontiumhydrate	$\text{Sr}(\text{OH})_2$	121.6
Strontiumnitrate	Nitricacid, strontiumsalt; strontiumdinitrate; strontium(II)nitrate(1:2)	$\text{Sr}(\text{NO}_3)_2$	211.6
Strontiumoxide	Strontia; strontiummonoxide	SrO	103.6
Strontiumperoxide	Strontiumdioxide	SrO_2	119.6
Strontiumphosphate	—	$\text{Sr}_3(\text{PO}_4)_2$	452.8
Strontiumsulfate	Celestine; celestite	SrSO_4	183.7
Strontiumsulfide	Strontiummonosulfide	SrS	119.7
Strontiumtitanate	—	SrTiO_3	183.5

2.3.2 Strontium in Water

ATSDR (2004) states that the natural weathering of rocks and soils and the discharge of wastewater release strontium directly into streams and aquifers. The settling of strontium dust out of the air constitute a very small part of the strontium found in water. According to ATSDR (2004), although the strontium is comparatively movable in water, the formation of insoluble complexes of strontium to soils can reduce its mobility.

According to Roskilde Amt (2005) report, strontium can also be released to the groundwater through the natural re-crystallizing of rocks. Elevated concentrations of strontium are available in low-groundwater-flow basins though high-flow basins may contain limited concentrations of strontium because it leaks out.

According to ATSDR (2004), deposition of strontium in marine carbonate sediment is the process by which strontium is removed from oceans since they are the largest reservoir of dissolved strontium. Some strontium returns to the terrestrial environment in the form of precipitation through sea spray. In different parts of the United States, Strontium has been measured in drinking water by the US-EPA to be less than 1 mg/l.

2.4 Boron and Strontium Toxicity

This section looks at studies concerning potential health effects and toxicity of boron and strontium.

2.4.1 Boron Toxicity in humans

According to Woods (1994), although the estimated average concentration of Boron in the Earth's crust is 10 ppm, the industrial revolution raised it up recently in the rivers of several borax-producing countries.

Most populations are exposed to boron through food. The food groups that are rich in boron include fruit, mushrooms, leafy vegetables, nuts and legumes. Meacham et al. (1998) found that meat and fish are low in boron, therefore, the ones who are mostly exposed to boron are the vegetarians. Rainey et al. (2002) reported a typical daily boron intake in the US population of 1.14 mg/day for men, 0.96 mg/day for women and a mean intake of 1.47 mg/day for vegetarian men and 1.29 mg/day for vegetarian women. Water can also be a rich source of boron especially water in large-scale borax mines which have been found to contain high boron concentrations.

Jansen et al. (1984); Usuda et al.(1998) state that there is a clear evidence that boron compounds can be digested in the human body. Boron is absorbed by animals and humans through the gastrointestinal tract. Over 90% of an orally administered boron dose is excreted in the urine in a short period of time by both humans and animals. According to Culver et al. (1994); Wilding et al. (1959) studies of boron miners indicate that it can be absorbed by inhalation.

Draize and Kelley(1959) indicate that boron is not absorbed dermally by humans or animals but can be absorbed through damaged skin tissue. According to Ku et al. (1991); Naghii and Samman (1996). Boron in the body exists as a dissociated boric acid and is distributed through the soft tissues. Ku et al.(1991); Chapin et al.(1997) state that Boron has a tendency to accumulate in bone, reaching higher accumulated levels after 1-4 weeks than those observed in plasma. According to the Institute for Evaluating Health Risks(1997); WHO(1998) states that boric acid is not degraded in the body but can form complexes with Bio molecules through concentration-dependent mechanisms

The effect produced by a continuous dose of boron in the reproductive organs is revealed through studies in laboratory animals. According to Seel and Weeth (1980), Fail et al. (1979), (1991), Linder et al. (1990), the results of their studies showed reduction in testis mass, atrophy, degeneration of the spermatogenic epithelium which reduces fertility and sterility.

Price et al.(1996); Field et al.(1989) report some other health effects such as high prenatal mortality, decreased fetal body mass, and malformations of the eyes, cardiovascular system and axial skeleton. Others symptoms of acute boron poisoning are nausea, vomiting, diarrhea, skin rashes and peeling of the epidermis. Harvey et al. (1975) state that in severe cases death occurs after 5 days by cardiovascular collapse and shock. According to Siegel and Wason(1986); Santé Canada(1990), the estimated lethal doses of boric acid are 15- 20 grams for adults and 5-6 g for children. However, no sufficient data linking boron exposure to cancer.

2.4.2 Boron Toxicity on mammalian sperm motility

The most important effect of the many studies that investigated the influence of boron exposure on the mammalian organism is boron's ability to disrupt the reproductive system reported by Cox(2004). It can seriously affect the reproductive system in mammals.

2.4.3 Boron Toxicity in plants

The rate of boron accumulation is related to tolerance in different plant species more than the resistance of tissues to the resulting toxicity is. In other words, some plants are more tolerant than others. Hilal et al.(2011) state that Boron is an important element in plant nourishment and growth, but there is an important micronutrient-toxic boron duality: a minimum concentration is required for the plant's survival but an excessive concentration produces negative influences and may cause poor performance in plant crops.

Hilal et al. (2011;56) state that in most crops, the symptoms of boron toxicity present as “burned edges on older leaves, yellowing of the leaf tips, accelerated decay, and ultimately death; the adverse physiological effects may also include reduced root cell division, retarded shoot and root growth, inhibition of photosynthesis, deposition of lignin and suberin, and reduced leaf chlorophyll.”

Nadav (1999) points out that the amount excess of boron and the tolerance level of the plant affect the appearance and severity of these effects .Generally, the quality of the irrigation water used and the soil boron content are the main reasons behind boron toxicity in plants. According to Rodriguez-Guerrero et al. (2009), the soil types that are derived from marine sediments and soils in arid or semi-arid regions where low rainfall results in very little leaching are the mostly affected types.

2.5 Strontium Toxicity

ATSDR (2004) states that there have been no bad effects of strontium on human health. However, some studies proved that it affects the human health causing lung cancer, for example. at extremely high concentrations, it is even known to cause cancer as a result of damage to the genetic materials in cells. strontium can also cause disruption of bone development when the uptake is extremely high.

2.6 Guidelines and Regulations

The World Health Organization (WHO) defines boron level of 2.4 mg/l in drinking water but the Strontium in the US Environmental Protection Agency (EPA) is 4 mg/l in drinking water. However, this percentage differs from one country to another in addition to the purpose of use whether for drinking or agriculture. Table 3 shows boron and strontium in drinking water guidelines through the world

Table 3 : Boron and strontium in drinking water guidelines through the world

Country/Organization	boron in Drinking Water	Strontium in Drinking Water	Unit
WHO	2.4	-	mg/L
EU	1	-	mg/L
Australia	0.3	-	mg/L
Israel	0.5	-	mg/L
Russia	-	4	mg/L
EPA	1	4	mg/L

2.7 A review of existing boron removal technologies

Yazicigil and Oztekin (2006) state that in the last ten years, specialists have used many techniques for boron removal, including electrodealysis used by Yazicigil and Oztekin (2006) precipitation used by Itakura et al. (2005), chemical coagulation and electro coagulation used by Yilmaz et al. (2007) and Koparal, et al. (2002), complexation /nanofiltration used by Dosoretz et al. (2006), phytoremediation used by Del Campo-Marin and Gideon (2007), ion exchange used by Simonnot et al. (2000) and Kabaya et al. (2004), reverse osmosis used by Prats et al. (2000) and Cengeloglu et al. (2008) and adsorption with different materials used by Öztürk et al. (2005) and Kavak (2009).

Boron separation technologies presently used around the world are mainly in use in seawater purification (desalination processes). According to Demey Cedeño, H. (2014), boron levels have been considerably reduced by thermal desalination (based on multi-stage flash (MSF) or multi-effect distillation (MED)) and membrane processes (including reverse osmosis (RO), ultra filtration (UF), microfiltration (MF) and nanofiltration (NF)).

Figure 2.1 (adapted from Ghaffour et al., 2013) shows the main desalination technologies currently in use around the world. More than 60% of the total is carried out using membrane process and 34.2% is performed using thermal processes. According to Ghaffour et al. (2013), the ongoing growth of the desalination market may make these figures constantly change.

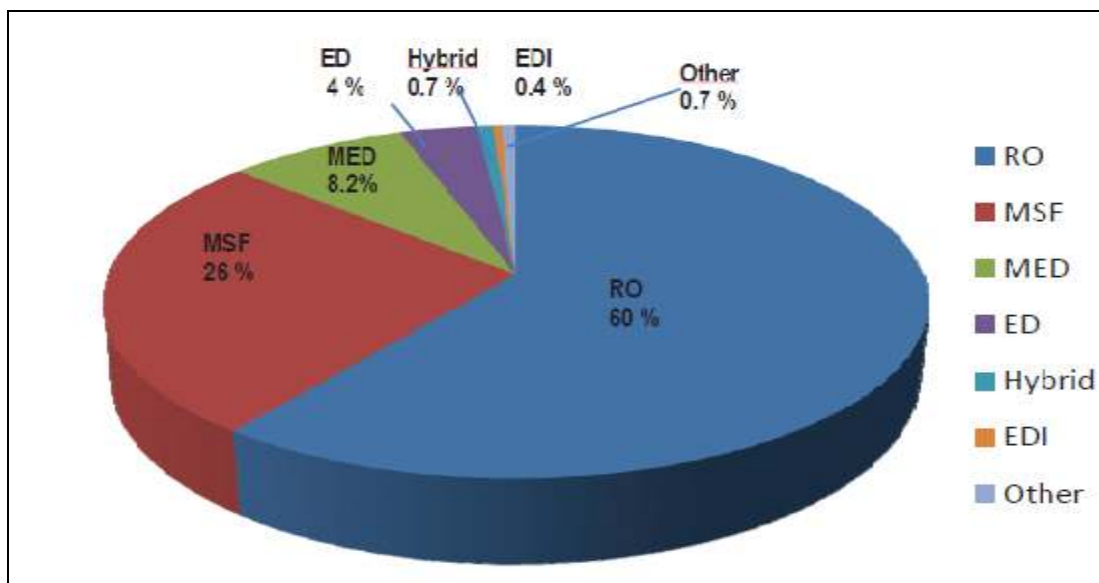


Figure 2. 1: Desalination technologies in current use. Adapted from the literature (Ghaffour et al., 2013)

According to Cedeño (2014), in various countries, there is an increased concern with efficient alternatives for boron removal from water. Due to that, research output on this subject has increased in the last five years, as shown in Figure 2.1. From 30 Scopus indexed publications in 2009, the figure grew to 68 in 2013, with a total of 231 indexed articles published as of April 2014 (for the period 2009-2014). Output is expected to increase even more in the future. In the period January-April 2014, the number of published articles was equal to total for the whole of 2009. Fifty one international patents were registered in the period 2009-2013, most of them for adsorption and membrane processes.

Notably, adsorption has been widely considered a good boron removal solution over the last five years. Cedeño (2014) points out that it has been the subject of the largest proportion of published articles. In other words, 35.5% of the Scopus indexed publications considered here deal with adsorption, 26.8% with membrane processes, 10.4% with hybrid membrane-sorption processes, and 27.3% with other techniques such as electro-coagulation, phyto-remediation, liquid-liquid extraction, chemical coagulation and precipitation. Figure (2.2.) Boron removal techniques addressed in published research over the last decade.

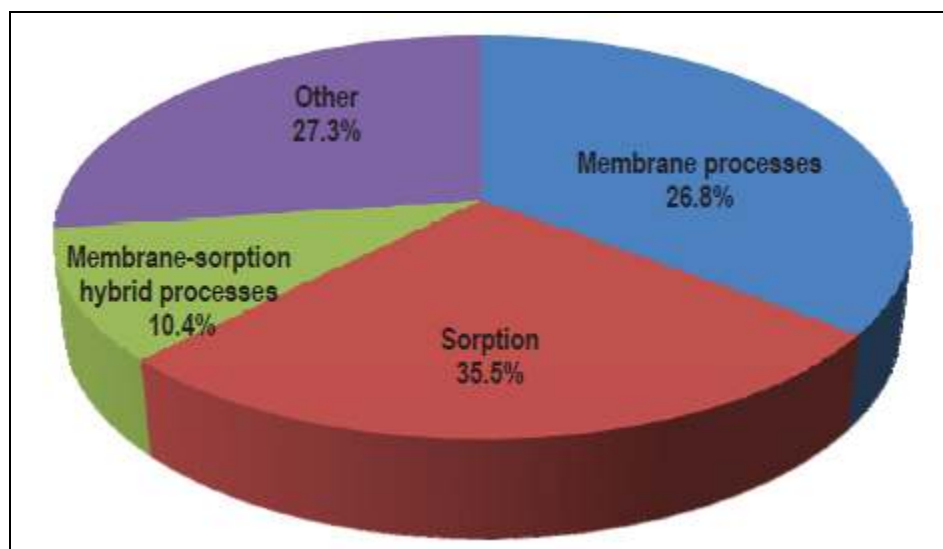


Figure 2. 2: Boron removal techniques addressed in published research over the last decade

Cedeño (2014) states that the significance of adsorption has increased in this field because of the low cost of the adsorbents used. Therefore, we can reutilize water materials that are treated as waste in many industrial processes to separate/recover boron. Studies using sepiolite by Öztürk et al. (2004), siral-30 and pural by Seki et al. (2006), bentonite by Karahan et al. (2006), red mud by Cengeloglu et al. (2007), ash by Öztürk et al. (2005) and impregnated carbon by Kluczka et al. (2007) have been performed.

Cengeloglu et al. (2008) have investigated the use of industrial waste sludge (red mud), which is rich in silica and aluminum, for the adsorption of boron from aqueous solutions, to find a reasonable option for the removal of boron compounds from industrial effluents. The performance of neutralized red mud has been examined as an adsorbent in terms of a function of variables such as pH (2-7), adsorbent mass dose (1-8 g/L), initial boron concentration (12-200 mg/L) and contact time (20-200 min). The results indicated that boron uptake increases as pH is increased; equilibrium was reached within 20 min.

Kavak (2009) investigated boron adsorption by using calcined alunite. He used a full factorial design (two levels) to examine the effect of temperature (25-45°C), pH (3-10) and mass of adsorbent dose (0.5 g and 1 g of adsorbent to 25 ml of solution). The findings of his study indicated that some factors affect boron removal such as boron uptake which increases when pH and the amount of sorbent are increased but decreases with increasing temperature. The optimum conditions were found at pH 10, adsorbent mass 1 g and temperature 25 °C; the maximum adsorption capacity obtained was 3.39 mg/g.

Similarly, Östürk and Kavak (2005) investigated boron adsorption using coal ash (fly ash). He studied the effect of pH, initial boron concentration, temperature, adsorbent mass dose and the presence of foreign ions on adsorption capacity. Fly ash was found to be efficient adsorbent for removing boron from aqueous solutions. The optimum operating conditions in a batch system were obtained at pH 2 and 25 °C, and the highest adsorption capacity obtained was 20.9 mg/g. The Langmuir isotherm equation suited the experimental equilibrium data and the pseudo-second-order model gave a better fit than the pseudo-first-order model in the kinetic study.

Chong et al. (2009) used a waste ash from the manufacturing process of palm oil (palm oil mill boiler, POMB) to study boron adsorption from ceramics industry effluents. Particle size was found to have an influence on sorption capability. He found out that a lower adsorbent particle size improved the boron removal. The best operating conditions were obtained with a particle size of 0.5 mm, 40 g of adsorbent in 300 ml of effluent (without pH adjustment), and an agitation speed of 100 rpm for 1 h. Through his study, he could reduce boron concentration from 15 mg/L to 3 mg/L. His main purpose behind this research was identifying a feasible alternative for boron removal from water and providing an application for residual ash from POMB in countries where palm oil production is plentiful.

2.8 A review of Existing Strontium Removal Technologies

According to (Gong et al. 2005), (Madaeni et al. 2004), and (Guibal et al. 2007), adsorption, ultra-filtration, coagulation–flocculation, ozonation, H₂O₂ oxidation, photo-oxidation Among are some of the different traditional techniques that have been used for pollutant removal among a combination of several techniques that have been applied. The cell walls of almond shell have also been used since they consist of cellulose, silica, lignin, carbohydrates which have hydroxyl groups in their structures. The potential of almond shell, an agro- based adsorbent, has been explored for the removal of Sr²⁺ from water.

(Mahmoodi 2013) sees that using adsorption process for Strontium removal is interesting because different adsorbents can concentrate specific substances from solution onto their surfaces. (Zhang et al. 2008) and (Lupa et al. 2016) point out that new materials were gained by impregnation of trihexyltetradecylphosphonium chloride (Cyphos IL-101) onto Florisil and Silica so that they can be used as adsorbent in the removal process of Sr²⁺ from aqueous solutions. The attained materials were characterized through FT-IR, SEM, EDX, and BET analysis. The adsorption

process has been investigated as a function of pH, solid:liquid ratio, adsorbate concentration, contact time and temperature. The isotherm data were well described by Langmuir isotherm model.

2.9 Olives production

The highly increasing need of olives lately helped the cultivation of olive trees grow more. This growth was a result of the increasing awareness of the benefits for the non-saturated vegetable oils. One of the most important benefits of olive oil is that it is a source of antioxidants, vitamin E, and monounsaturated fat which prevent cardiovascular. Olive oil also reduces the calorie intake. Table 4, shows the increase of the production for the period 2008 till 2013 in Gaza strip (source: Ministry Of Agriculture -Gaza - 2018).

Table 4 : The production olive for the period 2008 till 2018

No	Data / years	Area / Acres	Total output / ton
1	2008	25240	12294
2	2009	24051	2025
3	2010	27354	15386
4	2011	31780	18891
5	2012	33790	17271
6	2013	36430	10015
7	2014	31140	21010
8	2015	36383	14424
9	2016	36380	18191
10	2017	36440	20010
11	2018	36450	10001

2.10 Activated carbon

Activated carbon, also widely known as activated charcoal or activated coal is a form of carbon which has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. (Properties of Activated Carbon (n.d.)) Due to such high degree of micro porosity , just 1 gram of activated carbon has a surface area in excess of 500-1000 m² (about one tenth the size of an American football field), as typically determined by

nitrogen gas adsorption. Sufficient activation for useful applications may come solely from the high surface area (Merchant et al. (1993).

Activated carbons are widely used as adsorbents for the removal of organic chemicals and metal ions of environmental or economic concern from air, gases, potable water and wastewater (El-Hendawy,2003). There were many experiments to produce activated carbon such as Pistachio shell, coconut shell, rice husk, oil-palm shell, cotton stalks, wood, sugarcane bagasse, and many other agricultural wastes, but they failed because of the very low cost. (Logan et al. 2002).Activated carbon was also produced from cotton stalks by using the chemical activation method at 500°C. It was then cut and chopped and soaked in phosphoric acid for 22 hours. After that, it was dried in an electrical oven at 120°C for 6 hours.

Without any gas flow, the substance was carbonized and activated at 400-500°C. The pyrolyzed carbons were boiled in distilled water until the pH of the effluent water reached almost 6.5 and then dried in an electrical oven up to 100°C. This type of carbon was used in this study to investigate its efficiency in removing heavy metals (Louis,2006).

Ferro et al. (1990)19 made his experiments to use almond shells, olive stones, and peach stones to produce activated carbon in a CO₂ atmosphere at 850°C for almost 8 hours. He also studied the product on the adsorption of lead by using batch and column studies. In batch studies using 70 mg/l lead dose, the best removal capacity (22.7 mg/gm) was proved by the activated carbon produced from almond shells compared to the other two raw materials, the olive stone activated carbon yielding a capacity up to 18.3 mg/gm, and that from peach stones with a capacity of 17 mg/gm. The column study gave the same results as the batch study, where the activated carbon produced from almond shells was more effective for Pb removal than the other carbons.

Attia et al. (2004) has used cotton stalks to produce activated carbon. He investigated the adsorption of the produced activated carbon on the removal of nitrogen. Activated carbon was produced by using two different activation processes. The first is the chemical activation method that was adopted by leaving the cotton stalks in ZnCl₃ for 3 days, then activating the product at 600°C for 4 hours. The second process is the physical activation process which was used by pyrolysis at 600°C for 2 hours followed by steam activation at 950°C. The activated carbon produced from cotton stalks demonstrated good results for the removal of nitrogen.

Girgis et al. (1999) has used activated carbon to study the removal of nitrogen produced from cotton stalks. The chemical activation process has been used by passing H_3PO_4 at temperature $500^\circ C$ for 4 hours. This method produced high quality activated carbon. Many other studies are being checked out to discover other raw materials that are capable of producing activated carbon. Daifullah et al. (2003) has produced activated carbon from date pits, peach stones, almond shells, and olive stones with a high surface area equal $1100\text{ m}^2/\text{g}$ compared to the commercial one, and high micro pores area and total pore volume.

The raw materials used were: Coconuts and seed shell of palm tree (Gueu, et al., 2006), barley straw (Husseien, et al., 2008), Neem tree (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; Yeddou, et al., 2009), tamarind seeds (Munusamy, et al., 2011) and many other materials such as apple pulp, cane bagasse, 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.

In an inert atmosphere these materials were pyrolysed or carbobinized in order to remove volatile organic constituents, leaving a highly porous carbonaceous residue behind, followed by either chemicals or physical activation at a presence of Nitrogen, Steam or Carbon dioxide to rise the pores in the char (Carbonized Material). The preparation of activated carbons generally comprises two steps, physical and chemical activations (Yavuz et al., 2010) (Kopac et al., 2007).

2.10.1 Types of activated carbon

Current markets have three main types of activated carbon. These types are: powder, granular and pellet. There are many classification according to which activated carbon is classified which are its particle sizes and shape, and each type has its specific application. Figure (2.3) shows types of activated carbon; figure (2.4) shows powdered activated carbon; figure (2.5) shows granular activated carbon and figure (2.6) shows extruded activated carbon

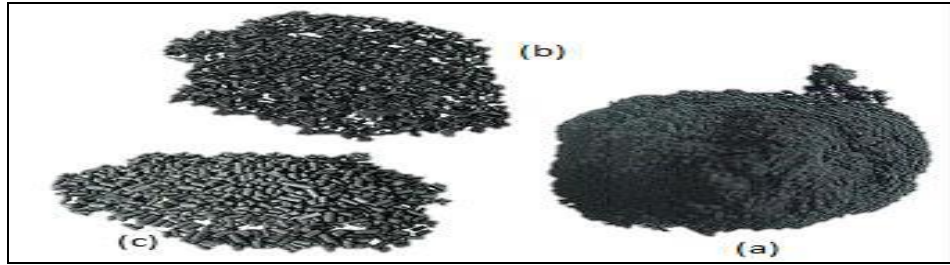


Figure 2. 3: Types of activated carbon



Figure 2. 4: Powdered activated carbon



Figure 2. 5: Granular activated carbon



Figure 2. 6: Extruded activated carbon

ASTM defined the types of activated carbon according to particles size . The powdered activated carbons (PAC) are derived from the chemical activation of carbon that has a particle size of 1 – 150 μm . The treatment of wastewater depends of this activated carbon. While granular (GAC) and extruded activated carbons (EAC), has particle size of 0.5 – 4 mm and 0.8 – 4 mm. Both GAC and EAC can be produced through the gas or physical activation and they are commonly used for the purification of gases.

2.10.2 Physical Activation

Physical activation process consists of two steps. It involves carbonization of raw material followed by activation at elevated temperatures in an inert atmosphere to eliminate oxygen and hydrogen elements as far as possible suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures or mainly volatiles (Bouchelta et al., 2008). Carbonization temperature ranges between 400 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$, The second stage involves thermal activation of this char. This can be done at the same temperature as or at a higher temperature and activation temperature ranges between 800 $^{\circ}\text{C}$ to 1100 $^{\circ}\text{C}$ (Román et al., 2008) (Al-Khalid et al., 1998)

2.10.3 Chemical activation

The preparation of activated carbon by chemical activation has only one step in which carbonization and activation is carried out simultaneously. At first, the precursor is mixed with chemical activating agent, which acts as dehydrating agent and oxidant. Chemical activation offers several advantages over physical activation which mainly include (i) lower activation temperature (< 800 $^{\circ}\text{C}$) compared to the physical activation temperature (800-1100 $^{\circ}\text{C}$) (Román et al., 2008), (ii) single activation step, (iii) higher yields, (iv) better porous characteristics, and (v) shorter activation times (Nowicki et al., 2008) .

Wet oxidation methods involve the reaction between the carbon surface and solutions of oxidizing agents such as phosphoric acid H_3PO_4 , nitric acid HNO_3 , hydrogen peroxide H_2O_2 , zinc chloride ZnCl_2 , potassium permanganate KMnO_4 , ammonium persulphate $(\text{NH}_4)_2\text{SO}_8$, potassium hydroxide KOH , etc. From the above oxidizing agents, phosphoric acid and zinc chloride are usually used for the activation of lingo cellulosic materials, which have not been carbonized before. On the other hand, potassium hydroxide is usually used to activate coal or chars precursors. It has been reported that zinc chloride produces activated carbon with higher specific area than that produced by using phosphoric acid.

The Coconut husk was activated 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 agent type has been checked in the study. The first step of the experiment started by locating the impregnation in a glass reactor fixed in the chamber of microwave oven that was connected to Nitrogen gas with a flow rate ($300\text{ cm}^3/\text{min}$) to purge air in the reactor before the start of microwave heating and continued to flow through activation. Potassium hydroxide was proved in the study to be a better activation agent regarding 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 (Foo, et al,2011).

Chemical activation was used to activate the char of Walnut shells and Olives stones by 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 researcher dried the mixture at $300\text{ }^\circ\text{C}$ for 3 hours 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.(Martínez, et al,2005).

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 $500\text{ }^\circ\text{C}$ 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 .(Moreno et al,2000).

2.11 Adsorption Process

By using activated carbon, sorption on solids is commonly used for purification in water and waste water. Adsorption is the accumulation of substances at a surface or interface. It could be occurring between liquid-liquid, liquid-solid, gas-liquid, or gas-solid. The material adsorbed or concentrated at a surface or interface of another medium is called adsorbate, while the adsorbing stage is known to be the adsorbent. The term sorption includes both adsorption and absorption

(Weber, 1972). Absorption is the interpenetration of the molecules or atoms of one phase with another to form a solution with the second phase.

In contrast, adsorption is the accumulating of something such as a gas, a liquid, or a solute, on the surface of a solid or a liquid. For example, the gas stripping (absorption) is used to achieve the removal of the undesirable dissolved gases from water or by adsorption onto a substance such as activated carbon. Adsorption commonly happens on account of a combination of two forces which are lyophobic (solvent disliking) and the affinity of the solute to the solvent. Thus, dissolved substances in aqueous systems are divided to either hydrophilic, water liking, or hydrophobic, water disliking. The hydrophobic substances tend to be adsorbed from the aqueous solution more likely than the hydrophilic ones (Weber, 1972). The adsorption rate depends on the mixing strength of solution, pH, nature of adsorbate, and temperature in addition to the cause of the adsorption, (Chen et al, 2001).

2.11.1 The Liquid – Solid Interface

The interaction of ions in the seawater with activated carbon components is subject to various types of factors. These factors are related with the properties of seawater (temperature, pH, Eh), the speciation of these actions and their concentrations, the structural characteristics of the activated carbon components like porosity, surface area, swelling, grain size, in addition to them, factors that include period of contact, degree of mixing and solid/liquid ratio. The adsorption process, takes place in four more or less definable steps: (1) bulk solution transport, (2) film diffusion transport, (3) pore transport and, (4) adsorption. Adsorption involves the attachment of adsorbate to adsorbent at an available adsorption site (Metcalf and Eddy, 2003). Figure (2.7) shows liquid – solid interface.

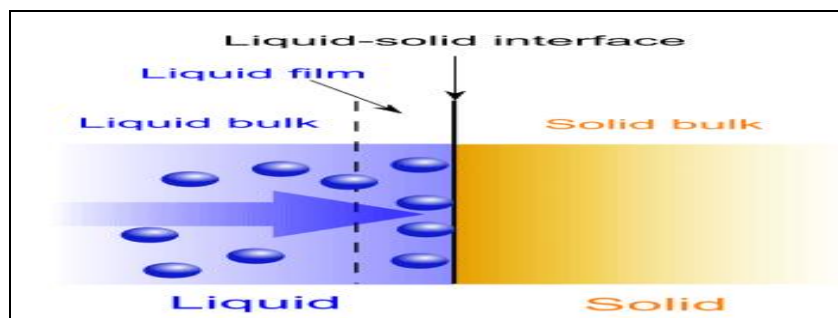


Figure 2. 7: Liquid – Solid Interface

2.11.2 Adsorption Isotherms

The adsorption isotherm is the term used to name the relation between amount adsorbed and concentration. Adsorption equilibrium data are typically plotted as an adsorption isotherm with the mass adsorbed on the y-axis and the mass in the fluid on the x-axis at constant temperature. The sorption isotherms are mathematical models that describe the distribution of the sorbate specie among liquid and solid phases, depending on a set of assumptions that are related to the heterogeneity/homogeneity of the solid surface, the type of coverage, and the possibility of interaction between the sorbate specie.

2.11.3 Boron Adsorption

It was reported that the adsorption method was economically promising for the removal of a minor constituent from a multi component solution. There had been many studies on the development of adsorbents for boron and its adsorptive properties. Activated carbon showed a high selectivity for boron among inorganic adsorbents. Some Previous attempts to remove boron from water were primarily based on boron specific ion exchange and second-cycle of RO desalination, yet these solutions add significant cost to the overall treatment technique (Nadav, 1999). In contrast, RO removes only afmtion of boron, between 40-65% (Magara, et.al., 1996, Pastor, et.al., 2001).

2.11.4 strontium Adsorption

Some Previous attempts to remove strontium from water were primarily based on strontium specific ion exchange. Some Previous attempts to remove strontium from wastewater using adsorption process is interested because different adsorbents are able to concentrate specific substances from solution onto their surfaces (Mahmoodi 2013). The cell walls of almond shell consist of cellulose, silica, lignin, carbohydrates which have hydroxyl groups in their structures. In this paper, the potential of almond shell, an agro- based adsorbent, has been explored for the removal of Sr^{2+} from water. (Gong et al., 2005; Madaeni et al 2004; Guibal et al 2007).

CHAPTER TREE
MATERIAL AND METHODS

CHAPTER THREE

MATERIAL AND METHODS

This chapter describes in detail material and methods producing activated carbon from crushed seeds, finds out its important characteristics, investigates the possibility of removing boron and strontium from standard solution and runs the experiment on samples collected from seawater.

3.1 Chemicals

During working on the project, several chemicals were used which were brought from Gaza's companies to be used in the lab. (Table 5) shows these chemicals along with their sources.

Table 5 : The Chemicals symbols, Molecular weight and sources.

No	Chemicals	Molecular Weight g/mol	Chemical Formula	Company
1	Potassium Hydroxide	56.11	KOH	HiMedia
2	Hydrochloric Acid	36.46	HCl	CARLO ERBA
3	Sodium Thiosulphate	158.11	Na ₂ S ₂ O ₃	Alpha Chemicals
4	Iodine	126.90	I ₂	HiMedia
5	Starch	162.16	(C ₆ H ₁₀ O ₅) _n	HiMedia
6	Sodium hydroxide	40	NaOH	HiMedia
7	Boric acid	61.83	H ₃ BO ₃	Oxford ChemServe
8	Strontium chloride(anhydrous)	158.53	SrCl ₂	Sigma
9	Potassium hydrogen phthalate	204.22	KHP	HiMedia

3.2 Instrumentation

Several devices were also used in the research phases. (Table 6) shows these equipment and instrument with their sources.

Table 6 : Instruments used in the research

No	Instrument	Company
1	Inductively Coupled Plasma-Optical Emission	SPECTRO GENESIS
2	Vacuum Desiccators	Thermo Fisher Scientific
3	Analytical balance	Adam
4	Portable pH/ORP/EC	Hach
5	Muffle Furnace	J.P Selecta Spain
6	Oven	J.P Selecta Spain
7	Shaker	J.P Selecta Spain

3.3 Preparation of Calibration Standard solution

Standard reference solutions (1000ppm) B and Sr were prepared from Boric acid and Strontium chloride. 10 ml each of standard reference solutions (1000ppm) was pipette into a 100 ml volumetric flask separately and diluted to volume with deionized water. This gave working standard solution with concentration of 100 ppm (solution A). Calibration standards for of B and Sr were prepared by adding appropriate volumes of standard working solution A with deionized water at 6 levels in the ranged between (0.25 , 0.5 , 1.0, 2.0, 5.0, 10.0 and 20.0) ppm.

3.4 ICP-OES Conditions

3.4.1 Inductively coupled plasma-optical emission

The ICP was developed for optical emission spectrometry (OES) by Wendt and Fassel at Iowa State University in the United States, and by Greenfield et al. at Albright & Wilson, Ltd. in the United Kingdom in the mid- 1960s. (Greenfield et al., 1965 ; C.B. Boss et al., 1997). The ICP is

now not only the most popular source for OES but also an excellent ion source for mass spectrometry: inductively coupled plasma mass spectrometry (ICP-MS). (V.A. Fassel 1986)

3.4.2 Inductively coupled plasma operation

As shown in Figure (2.8), the so-called ICP torch is usually an assembly of three concentric fused-silica tubes. These are frequently referred to as the outer, intermediate, and inner gas tubes. The diameter of the outer tube ranges from 9 to 27 mm. A water-cooled, two- or three-turn copper coil, called the load coil, surrounds the end of the torch and is connected to an RF generator. The outer argon flow (plasma gas, $10\text{--}20\text{Lmin}^{-1}$) sustains the high temperature plasma and positions it relative to the torch outer walls and the induction coil, preventing the walls from melting and facilitating the observation of emission signals. Under these conditions, the plasma has an annular shape. The sample aerosol carried by the inner argon flow (nebulization gas, $0.5\text{--}1.5\text{Lmin}^{-1}$) enters the torch central channel and helps to sustain the plasma shape. The intermediate argon flow (auxiliary gas, $0\text{--}1.5\text{Lmin}^{-1}$) is optional and may serve the functions of diluting the inner gas flow in the presence of organic solvents, or pushing the plasma slightly away from the end of the central sample tube, improving the transference of energy from the plasma to the sample aerosol. The auxiliary gas plays an important role while running high total dissolved solid (TDS) samples and organic solvents. of salt and carbon particles on the torch and the preoptics.

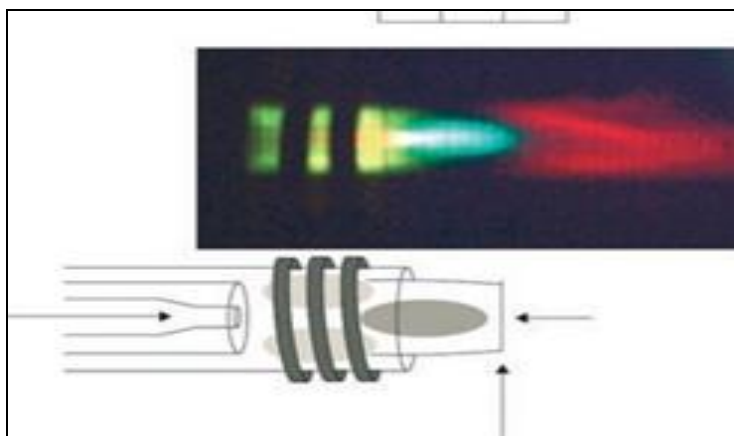


Figure 3. 1: Schematic diagram and actual photograph of an ICP assembly

3.4.3 Inductively Coupled Plasma Characteristics

The main analytical advantages of the ICP over other excitation sources originate from its capability for efficient and reproducible vaporization, atomization, excitation, and ionization for a wide range of elements in various sample matrices. This is mainly due to the high temperature,

6000–8000 K, in the observation zones of the ICP, which is much higher than the maximum temperature of flames or furnaces (3300 K).

The high temperature of the ICP also allows it to excite refractory elements and renders it less prone to matrix interferences. Other electrical-discharge-based sources, such as alternating current and direct current arcs and sparks, and the microwave-induced plasmas (MIP) also have high temperatures for excitation and ionization, but the ICP is typically less noisy and better able to handle liquid samples. In addition, the ICP is an electrodeless source, so there is no contamination from the impurities present in an electrode material. Furthermore, it is relatively easy to build an ICP assembly, and it is inexpensive when compared to some other sources such as a LIP.

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) with radial torch equipped with argon saturation assembly was used for the determination of lead and cadmium. High purity (99.99%) argon was used as plasma, auxiliary and nebulizer gas. The gas flows were kept at 15.0 l/min for plasma, 1.50 l/min for auxiliary and 0.56 l/min for nebulizer. Radio frequency (R.F) power of the plasma generator was 1.35 kW. Vertical height of the plasma was fixed at 7 mm. Sample uptake time of 30.0 sec, delay time of 5 sec, rinse time of 10 sec, initial stabilization time of 10 sec and time between replicate analysis of 5 sec.(Sen, et al,)

3.5 Samples Collection

The Olive Seeds sample used in this study were obtained from olive mills in the Gaza Strip (Dalol olive mills) . Fresh representative samples of olive mills were collected directly at the outlet of the grinding machine. Figure 3.1 shows olive seeds samples collection.



Figure 3. 2: Olive seeds samples collection

3. 6 Carbonization of the Olive Seeds

OS waste was obtained from Gaza, Palestine. The OS waste was rinsed thrice with hot water, thrice with cold water as figure (3-2), (3-3) and (3-4) below show.



Figure 3. 3: Cleaning and preparation of crushed olive seeds

Then, it was dried in an oven at 105 °C for 24 h to remove moisture content. Once dried, they were ground and sieved for a particle size of 2.0 mm to 3 mm (Alslaibi et al,2013).



Figure 3. 4: Preparation of crushed olive seeds in oven



Figure 3. 5: crushed olive seeds after the oven

Carbonization step was carried out at 600°C for 1 h under purified nitrogen (99.99%) (Demiral, et al.,2011) and Aljundi, et al., (2008). The coming points were recognized through carbonization (Ashour ,2013):

1. Control the flow of nitrogen with a range 300 to 500 cm³/min.
- 2.It was hard to make the temperature under the rate of 35°C /min because the research depended on an gaseous energy oven not an electrical one.
- 3.The steam began to arouse of the sample after 5 minutes from starting at temperature of 200°C /min. some drops of water were also noticed.
- 4.Twelve minutes after starting, at about 500°C , the smoke started to release from the outlet and the drops of water (Black viscous) came out of the tube.
- 5.It continued to smoke for 8-10 minutes then stopped after that.
- 6.It stayed the same after 10 more minutes at 500°C.

3.7 Activation of the Char

There are different ways of activation, chemical, physical and microwave. Every procedure has its advantages and disadvantages, the activation by using a chemical activation agent such as potassium hydroxide (KOH) was used to activate the char because KOH appears to be the best activation agent in terms of both adsorption capacity and carbon yield (Foo et al, 2011) and (Martinez, et al, 2005) and (Foo et al, 2011) . The amount of KOH used was modified to give a specific Impregnation ratio(weight of activating agent: weight of char) of 1.25:1w/w(Moreno-Castilla , et al., 2000).

The activation of KOH-impregnated char was carried out at different temperatures ranging from 650°C to 750°C under a nitrogen flow of 150 cm³/g and at a heating rate of 10°C min⁻¹ in a vertical muffle furnace. After activation, the samples were cooled down under the nitrogen flow and were washed sequentially several times with hot deionized water (70°C) and HCl (0.1 M) until the pH of the washed solution was within the range 6.5 to 7. Finally samples were dried in an oven at 110°C for 24 h and then stored in containers.

3.8 Characterization of Activated Carbon

It's very important to characterize the activated carbon to classify AC for particular uses. There's the AC that is characterized physically or chemically. The physical and the chemical properties of the raw materials affect the characteristics of the activated carbon in addition to the activation method that was used as stated by (Guo et al,2003) . The use of a granular AC can be affected by physical properties like ash content and moisture. They can make them suitable or unsuitable for particular applications.

3.8.1 Moisture Content

The activated carbon moisture content may be expressed by weight as the ratio of the mass of water present to the dry to the dry weight of the AC sample ,To determine any of these ratios for a particular AC sample, the water mass must be determined by drying the AC to constant weight and measuring the AC sample mass after and before drying. The water mass (or weight) is the difference between the weights of the wet and oven dry samples. The criterion for a dry AC sample is the AC sample that has been dried to constant weight in oven at temperature between 100 – 110 °C (105°C is typical)the method of (Rengaraj et al,2002).

3.8.2 Volatile matter content

A crucible was pre-heated in a muffle furnace to about 900°C, cooled in a desiccator and weighed. 1.0g of activated carbon samples were transferred into the crucibles and reweighed. The crucibles containing the samples were then placed in a cold muffle furnace and the temperature was allowed to rise to 900°C it may take from 7 minutes. It was removed and allowed to cool in a desiccator to room temperature and reweighed again (ISO 562-1981). The weight of the sample before heating and after heating was used to determine the amount of volatile matter present in the sample. Larger weight loss of the substance implies greater volatile matter content. The ash content was calculated using the equation.

$$\text{Volatile matter content (\%)} = \frac{\text{weight of volatile component (g)}}{\text{oven dry weight}} \times 100$$

3.8.3 Ash content

The ash content of a carbon is the residue that remains when the carbonaceous and activation materials is burned off. Ash content can lead to increase efficiency of the activated carbon. A crucible was pre-heated in a muffle furnace to about 650°C, cooled in a desiccator and weighed. 1.0g of activated carbon samples were transferred into the crucibles and reweighed. The crucibles containing the samples were then placed in a cold muffle furnace and the temperature was allowed to rise to 650°C it may take from 4 to 10 hours. It was removed and allowed to cool in a desiccator to room temperature and reweighed again. In this test, the amount of residual substance is equal to the ash present in the sample (ASTM D2866-94).

$$\text{Ash content (\%)} = \frac{\text{Ash weight (g)}}{\text{Oven dry weight (g)}} \times 100$$

3.8.4 Iodine number

To gain further knowledge of the porous structure of activated carbon, iodine adsorption from liquid phase was adopted by other researchers (Martinez et al,2005) . The adsorption of aqueous I₂ is considered a simple and quick test for evaluating the surface area of activated carbons associated with pores larger than 1 nm. (Bac et al,2001) The iodine value, defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration of 0.02N (ASTM 2006). Iodine Number is accepted as the most fundamental parameter used to characterize activated

carbon performance. It gives the measure of activity level (higher number indicates higher degree of activation).

Reagents used in the iodine value test are as listed below:

(0.1N Iodine solution -0.05N Sodium Thiosulphate -1% Starch solution -Activated carbon)
calculated as amount of iodine number in milligrams.

$$\text{Iodine number} = \frac{(\text{blank} - \text{sample})}{\text{blank}} \times \frac{(V \times 0.1N)}{\text{mass of activated carbon}} \times 253.81$$

Where 253.81 is the atomic mass of iodine and V is 20ml aliquot.

3.8.5 Bulk density

The density is important parameter when an activated carbon product is to be investigated for its filter ability . The density of the prepared activated carbon was determined by weighing (10cm³) of carbon sample using graduated cylinder. 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, and ASTM D 2854).

$$\text{Bulk density } D_b = 1000 \frac{M}{V}$$

(V) The procedure is repeated until the difference between the two observation.

(M)The weight of the content of the cylinder.

3.8.6 pH

1 g of the sample was weighed and dissolved in de-ionized water. The mixture was heated and stirred for 3 minutes cool at room temperature. The solution was filtered and determined using a digital pH meter .

3.8.7 Surface area

Generally, the larger the specific surface area of the adsorbent, the better its adsorption performance will be (Guo et al,2003)(Glasstone et al,1983) . The most widely used commercial active carbons have a specific surface area of the order of 600- 1200 m²/g (Ng et.al, 2002). The pore volume limits the size of the molecules that can be adsorbed whilst the surface area limits the amount of material which can be adsorbed, assuming a suitable molecular size (Lartley et.al, 1999).

The adsorptive capacity of adsorbent is related to its internal surface area and pore volume. The specific surface area (m^2/g) of porous carbon was determined according to Langmuir Isotherm test which is summarized in the following steps as it is clear in the reference research (El-Hamouz, et al., 2006).

1. Taking seven samples of the activated carbon each weighted 1 gram and placed it into the pretreated bottles.
2. A range of acetic acid concentrations was prepared between 0.015 to 0.15 M(C_0)each 100 ml and place it into the bottles where the activated carbon was placed.
3. Thermostat at 25°C the bottles are kept and periodically shaking the bottles for 60 minutes until reach equilibrium.
4. Filter the samples and eliminate the first 10 ml and titrate using NaOH 0.1 M and Phenolphthalein, KHP was used standardization of sodium hydroxide solutions .
5. 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 $N = (C_0 - C_e) \cdot V/g$ (V : volume of samples, g grams of activated carbon, C_0 : Initial Concentration, C_e : Final Concentration at equilibrium).
6. A graph is plot for C_e Vs C_e/N , according to the equation $C_e/N = C_e/N_m + 1/kLN_m 1/N_m$ is the slope of the curve is giving the number of acetic acid moles adsorbed by a gram of activated carbon, $1/KL$ is a constant equal the intersection from the Y axis as shown in Figure 3-5 .
7. Assuming a mono layer of acetic acid and knowing the molecule as $2.1 \times 10^{-19} \text{m}^2/\text{molecule}$ and Avogadro's number is $6.02 \times 10^{23} \text{molecule/mole}$, the total area is calculated.

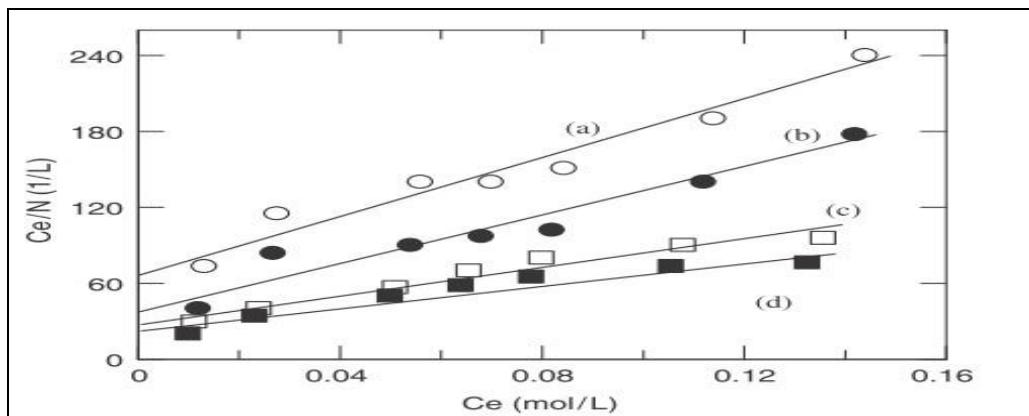


Figure 3. 6: Langmuir plots for acetic acid adsorption onto AC with different

3.9 Commercial Activated Carbon

The company manufactured performed many experiments to determine the characteristics of the activated carbon product and it was the most important tests to measure the surface area of a commercial type with a well-known surface area measured by BET N₂ to test the performed procedure and find out the correction factor for the following measurements on the produced activated carbon. Following is in Table (7) the characteristics of the commercial activated carbon as described by the manufacturer (Jacobi Carbon – Aqua-Sorb 2000).

Table 7 : Characteristics of Commercial Activated Carbon (Jacobi Carbon –Aqua-Sorb 2000)

Parameter	Unit	Value	Test Method
Iodine number	mg/g	1050	ASTMD4607
Surface area	m ² /g	1100	BETN ₂
Methylene blue	mg/g	280	JACOBIT4001
Total pore volume	cm ³ /g	1.04	Porosimetry (N ₂ /Hg)
Apparent density	Kg/m ³	470	ASTMD2854
Bed density, back washed and drained	Kg/m ³	410	Note 1
Wettability	%	99.5	JACOBIT4003
Moisture content- as packed	%	2	ASTMD2867
Water soluble matter	%	0.2	ASTMD5029
pH		8	ASTMD3838
Chlorine half length value(12x40USS)	cm	2.2	DIN19603
Ball-pan hardness number	%	95	ASTMD3802
Note1: Value is based on the back washing of a bed of Aqua Sorb@2000 activated carbon at 30% expansion, which has been allowed to drain and settle.			

3.10 Removal of Boron and Strontium by Produced Activated Carbon

Boron and strontium are generally distributed in the environment, occurring naturally or due to anthropogenic contamination (Simonnot, et al., 2000). Though boron and strontium are essential micronutrient for plants and animals including humans, the line between deficiency and excess is narrow and excessive amount of boron and strontium could have negative effect on health and plant . The percentage removal of Boron and strontium at the sea water depends on the pretreatment process for the RO-Plants, which will help in completing the desalination of the sea water without passing to the second pass of membranes.

Data collection to find out the concentration of boron and strontium in sea water classifying these boron and strontium chemically, Through this thesis an experimental study will find out the concentration of strontium and boron in sea water from Gaza. has been done at CMWU laboratory. In the analysis findings the average concentration of strontium in sea water is approximately 8.1 mg/L and concentration of boron are found in seawater 4.8 mg/l . Strontium and the Boron concentrations have been tested using Inductively coupled plasma(SPECTRO GENESIS ICP-OES) in CMWU laboratory .



Figure 3. 7: Inductively coupled plasma in CMWU laboratory

3.11 Batch Experiments with activated carbon

In batch adsorption experiments known different weights of AC (0.5, 1, 2.5, 5 and 10 g) were added to polyethylene tubes containing 50 mL boric acid (H_3BO_3) solution containing 8 mg/L boron at room temperature but the standard solution for Strontium is Strontium chloride ($SrCl_2$)($SrCl_2 \cdot 6H_2O$) containing 10 mg/L Strontium at room temperature and shaker at approximately 600 rpm. The contact time was changed from 10 minutes to 24 hours . The contents were filtered with membrane filters 0.45 μ m, boron and strontium were determined by using ICP-OES.

3.12 Effect of pH

The pH of the solution is an important factor for the removal of boron and strontium by activated carbons. Tested olive seeds based activated carbons for the removal of boron and strontium at different pH values ranges from 2.0 to 8.0. They observed that the adsorption of heavy metals continuously decreased with the increase in pH and the maximum adsorption was observed at pH 2.0. Similar results were also obtained by (Goswami et.al,2005) and (Karthikeyan et .al,2005) (Tang et.al,2009) .

3.13 Effect of Time

It can be seen that AC adsorption is very rapid during first 10 min of adsorption. After 5 hr , AC adsorption nearly reached the equilibrium value. This speedy adsorption of AC and reaching at equilibrium in a short period indicates the efficacy of the AC adsorption.

3.14 Effect of Temperature

In this section, the effect of temperature on the efficiency of boron and strontium removal .

3.14.1 Boron (B)

The fact that temperature plays a pivotal role in the sorption process has been taken for granted. The sorption of AC on the boron was investigated in the range of 25–40°C. The adsorption process depends mainly on the quantity of adsorbent. Physical condition such as temperature was investigated in this part. Figure 4-9 clarifies the relationship between temperature for adsorption of B ions and the adsorbent. Temperature was observed to check its effect on boron removal efficiency (Aksu et.al, 2008).

3.14.2 Strontium (Sr)

Temperature has an obvious influence on sorption. So as to investigate the effect of temperature, the sorption of Sr ions onto composite adsorbent was investigated in the temperature range of 25–40°C under optimized conditions .Figure (4.10) explains the relationship between temperature for adsorption of Sr ions . (Yusan, et.al, 2011).

3.15 Effect of adsorbent dosage

The effects of different adsorbent dosages (g) on Boron and Strontium percent removal. The increase in Boron and Strontium removal with adsorbent dosage can be attributed to an increase in the adsorbent surface, which increased the availability of adsorption sites. However, if the adsorption capacity (mg/g) decreased with the increasing amount of adsorbent. The decreased is due to adsorption sites remaining unsaturated during the adsorption process (ChaoYin et al., 2008).

CHAPTER FOUR

RESULTS AND DISCUSSION

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Carbon Characterization

4.1.1 Surface Area

Surface areas were measured using the adsorbed acetic acid method. This method has low accuracy, also it has low efficiency to measure the internal surface area of AC.

4.1.1.1 Commercial activated carbon

The resulted isotherm graph for the acetic acid and produced activated carbon is as shown in figure 4.1.

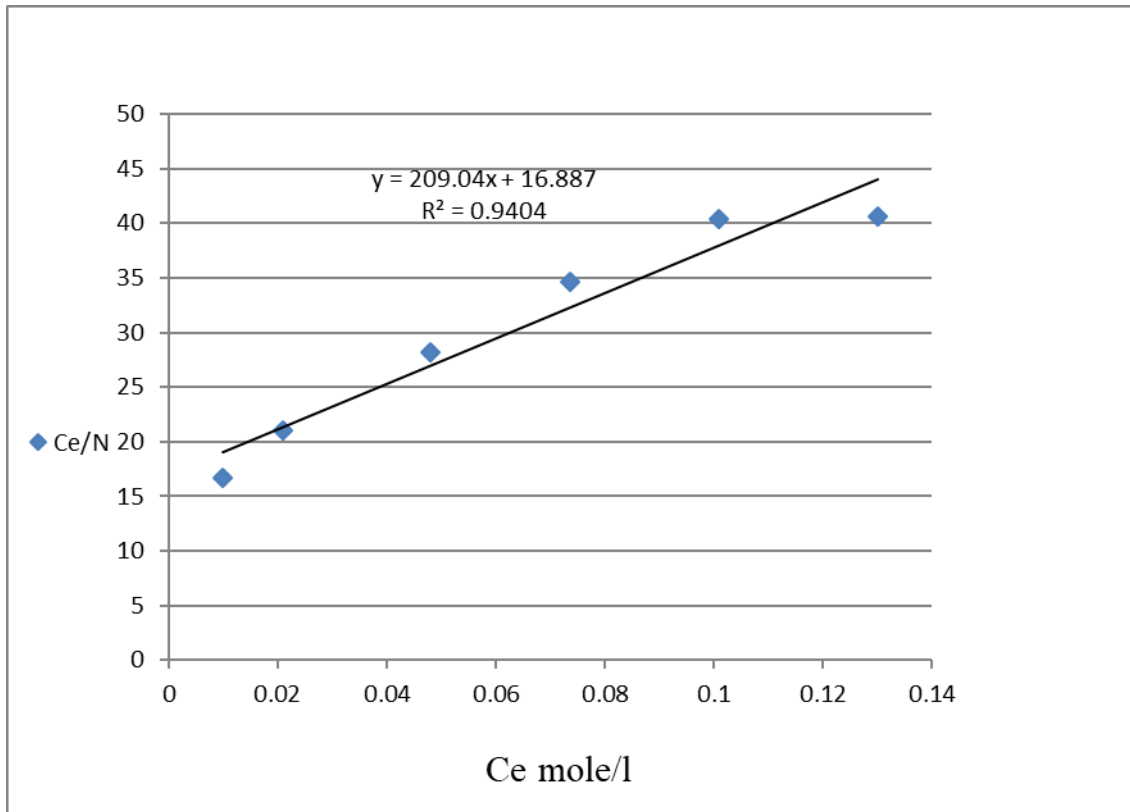


Figure 4. 1: Acetic Acid Commercial Activated Carbon Isotherm

The measured surface area by acetic acid Isotherm is 605 m²/g, while the surface area measured by the manufacturer by BET N₂ is 1100 m²/g therefore, a factor of 1.81 was considered to find out the BET N₂ of the produced activated carbon.

4.1.1.2 Produced activated carbon.

Therefore, the measured values of the surface areas should be considered as approximate ones. Plots of C/N versus C were constructed according to equation earlier as shown in (Figure 4.2). The surface area of adsorbent was then calculated as explained earlier .

The resulted isotherm graph for the acetic acid and produced activated carbon is as shown in figure 4-2. The surface area of adsorbent was calculated as explained the BET N2 surface areas for AC result is $681.5 \text{ m}^2/\text{g}$ with $R^2 = 0.983$.

This Value confirmed that the adsorption of acetic acid on the surface of AC. Follow the Langmuir isotherm.

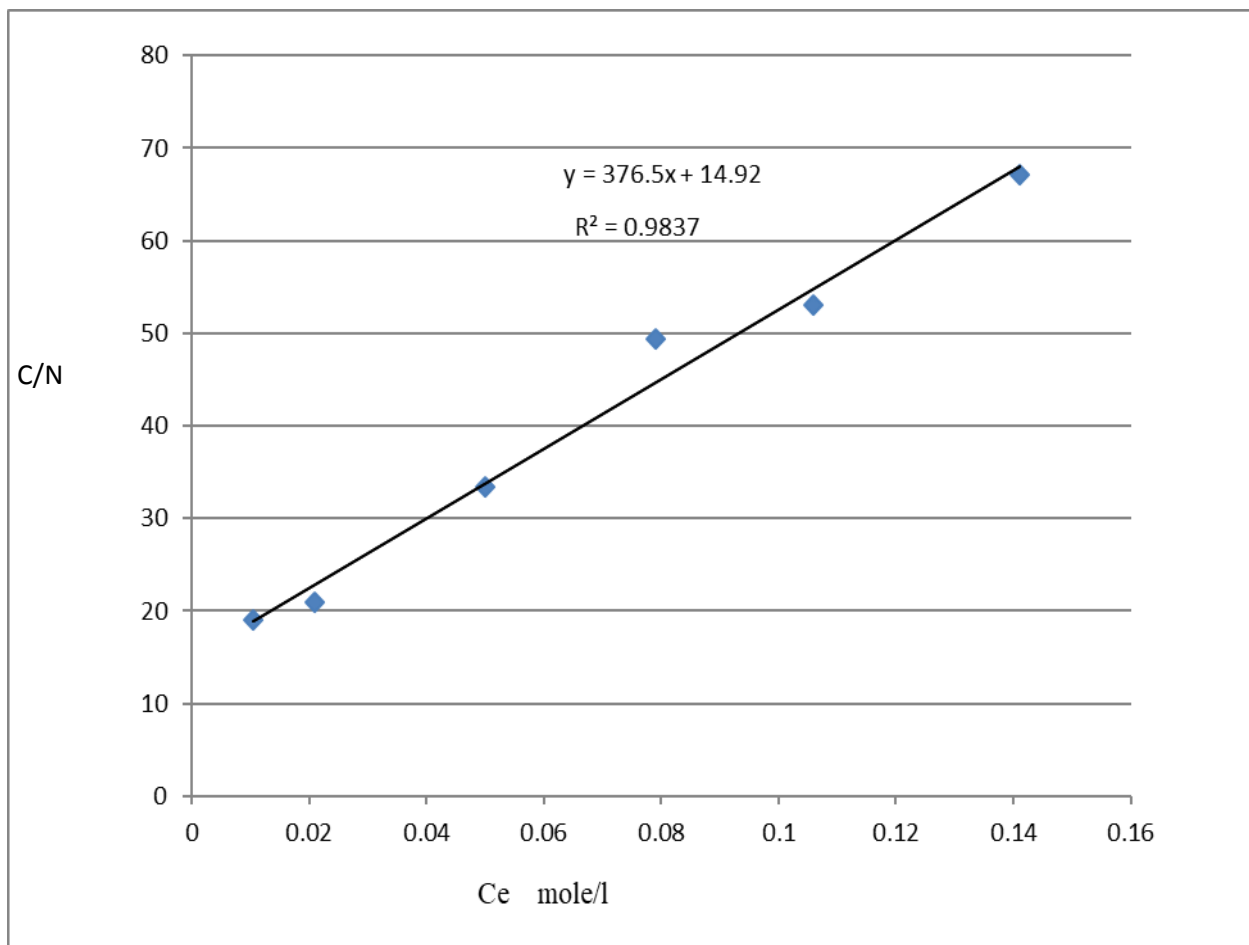


Figure 4. 2: Langmuir plots for acetic acid adsorption onto AC. All experiments were conducted at room temperature using 1.00 gm AC

4.1.2 Ash Content and Volatile Matter Content

The average Ash content of the produced activated carbon is 2.21 ± 0.05 %. The table 7 shows the results.

Table 8 : Ash content calculation

Sample NO.	Sample wt.	Wt of ash.	Ash content.
	g	g	%
1	1.05	0.024	2.29
2	1.04	0.023	2.21
3	1.02	0.022	2.16
Average Ash content			2.21 ± 0.05

Table (8) ash content calculation shows a low amount of ash content, Ash content can also affect activated carbon i.e. it reduces the overall activity of activated carbon. It also reduces the efficiency of reactivation, the lower the ash value therefore the better the activated carbon for use as adsorbent. generally, ash content between 2 and 10% .

4.1.3 Volatile matter content

The average volatile matter content of the produced activated carbon is 2.21 ± 0.05 % .

The lower the volatile matter content therefore the better the activated carbon for use as adsorbent.

4.1.4 Bulk density

The density is important parameter especially when an activated carbon produced. This is because it determines the mass of AC that can be contained in a filter of given solids capacity and the amount of treated liquid that can be retained by the filter . The results of measuring the density for the samples is $0.745 \pm 0.02 \text{g/cm}^3$.According to AWWA, (1991), lower limit of bulk density is 0.25g/cm^3 .

4.1.5 Iodine number

The iodine number obtained for the sample was 1042mg/g . It is known that activated carbon do adsorb iodine very well and hence the iodine adsorption number is a good indication of

the total surface area of the activated carbon. It is a measure of activity level, the higher iodine number the more activation efficiency.

4.1.6 pH

The pH affects the activated carbon adsorption . The value of pH obtained is 6.90. Activated carbon is more effective at low pH than high pH.

4.1.7 Moisture content

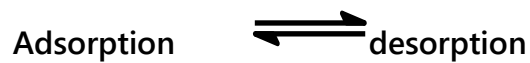
The results of measuring the Moisture content for the samples was the result values is 3.62% . The moisture content does not affect the adsorptive power of activated carbon.

4.2 Boron and Strontium Removal

Various operational parameters was tested in order to determine the feasibility of using activated carbon materials for removal boron and strontium .As referenced previously in chapter three these include pH , time , temperature and adsorbent dosage .

4.2.1 Effect of time

It is observed that the rate of increase removal of boron and strontium by the produced activated carbon with increase the time. It is also observed that the rate of removal for boron by use produced activated carbon in the 12 hours (85%). Adsorption increased by increasing concentration of limiting value about 85% after 12 hr the decrease due to desorption of B from the surface of AC, this indicate that equilibrium process is occurred between the adsorption and desorption.



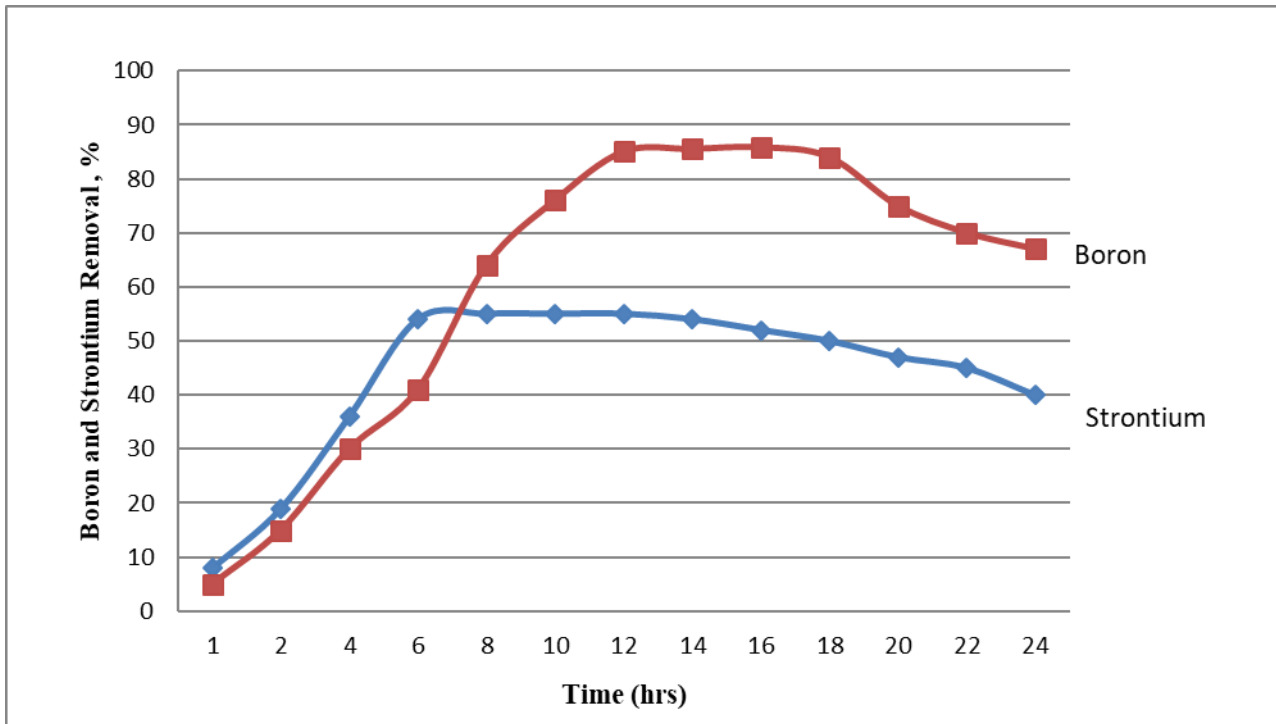


Figure 4. 3: Effect of time on removing boron and Strontium from synthetic solution

For strontium was observed that the rate of removal amount in the first 6 hours (55%). Adsorption increased by increasing concentration of limiting value about 55% after 6 hr the decrease due to desorption of Sr from the surface of AC, this indicate that a saturation process is occurred between the adsorption and desorption.

4.2.2 Effect of Concentration

A series of experiments were performed at different initial adsorbate concentrations, viz., 1, 5, 7 and 10 mg/L, at room temperature and natural pH. The results are given in Figure 4-4 and 4-5. It can be seen that increasing the initial concentration is accompanied by a decrease in the percentage adsorption of boron and causing a delay in the attainment of equilibrium.

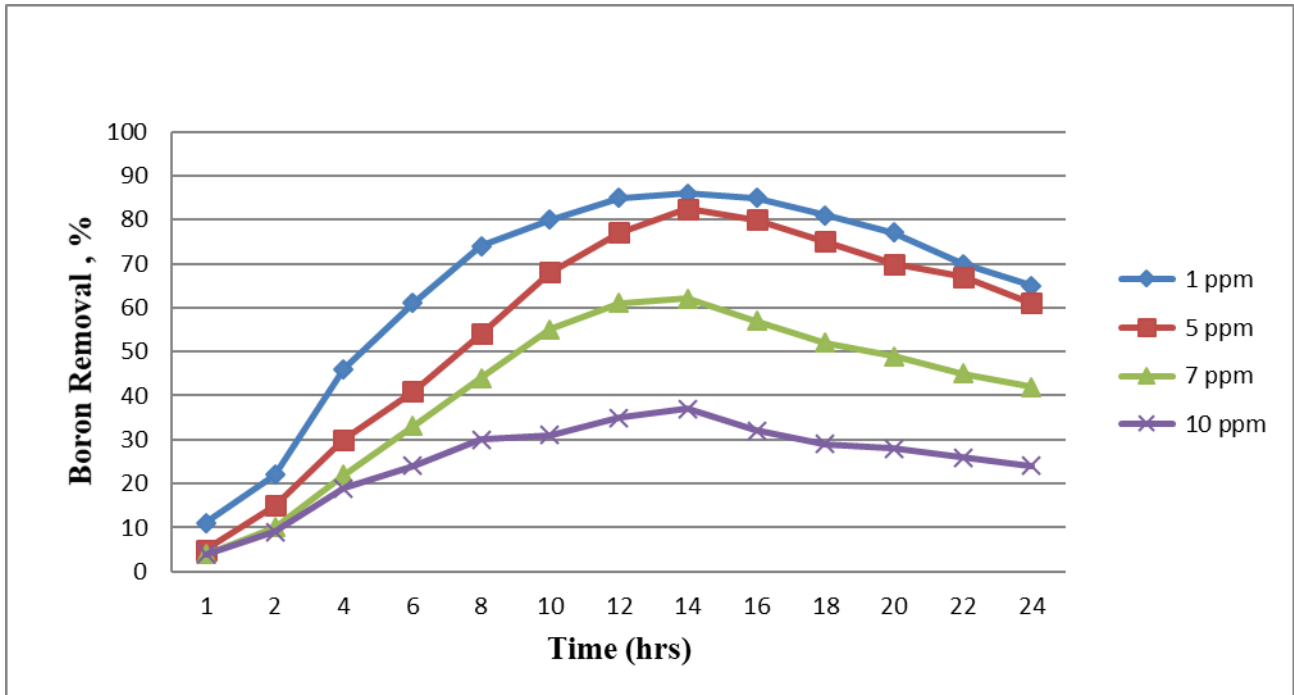


Figure 4. 4: Effect of Concentration on removing boron from synthetic solution

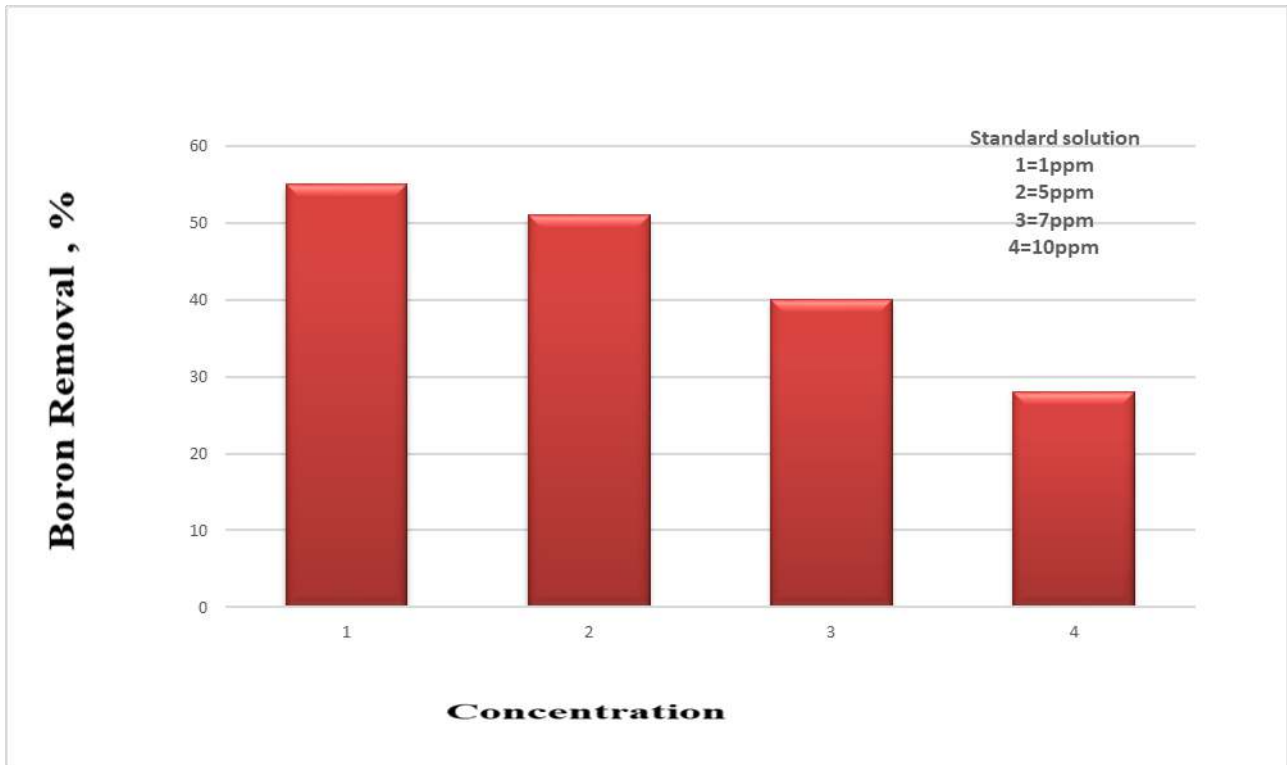


Figure 4. 5: Effect of Concentration on removing boron from synthetic solution at maximum removal

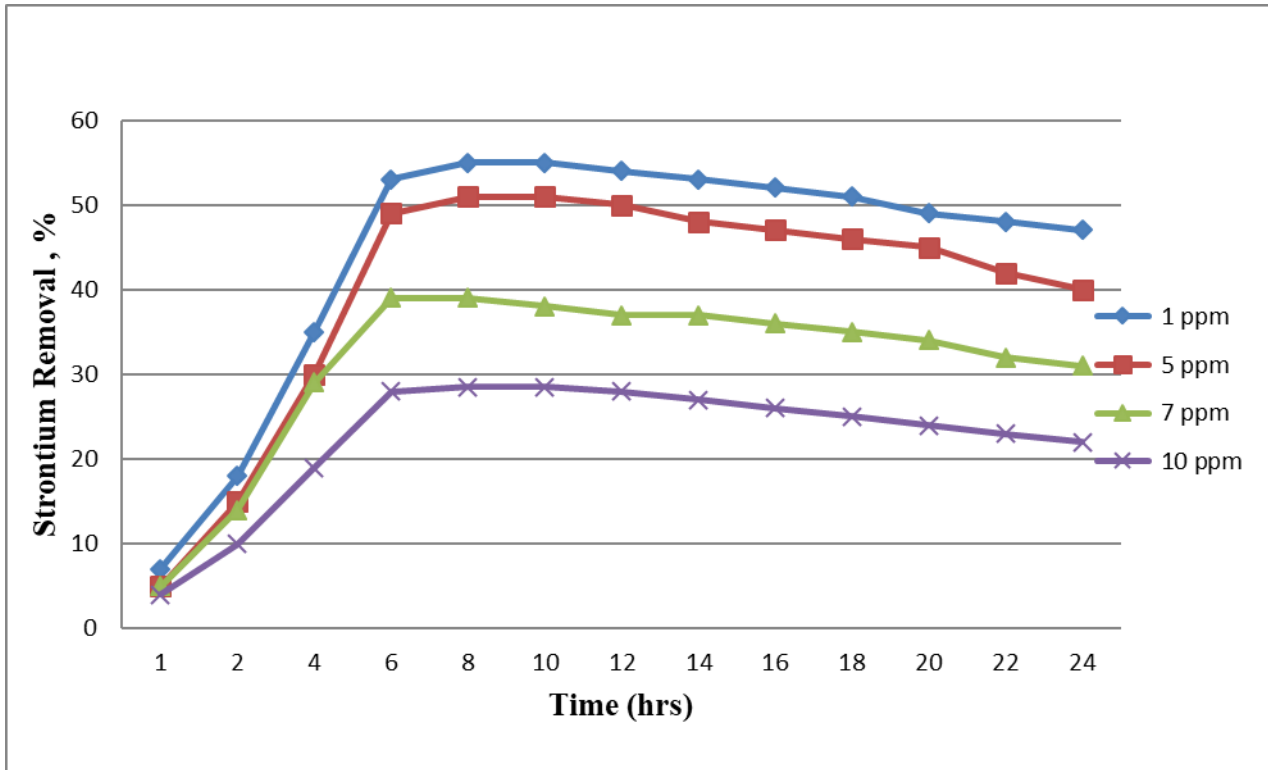


Figure 4. 6: Effect of Concentration on removing Strontium from synthetic solution

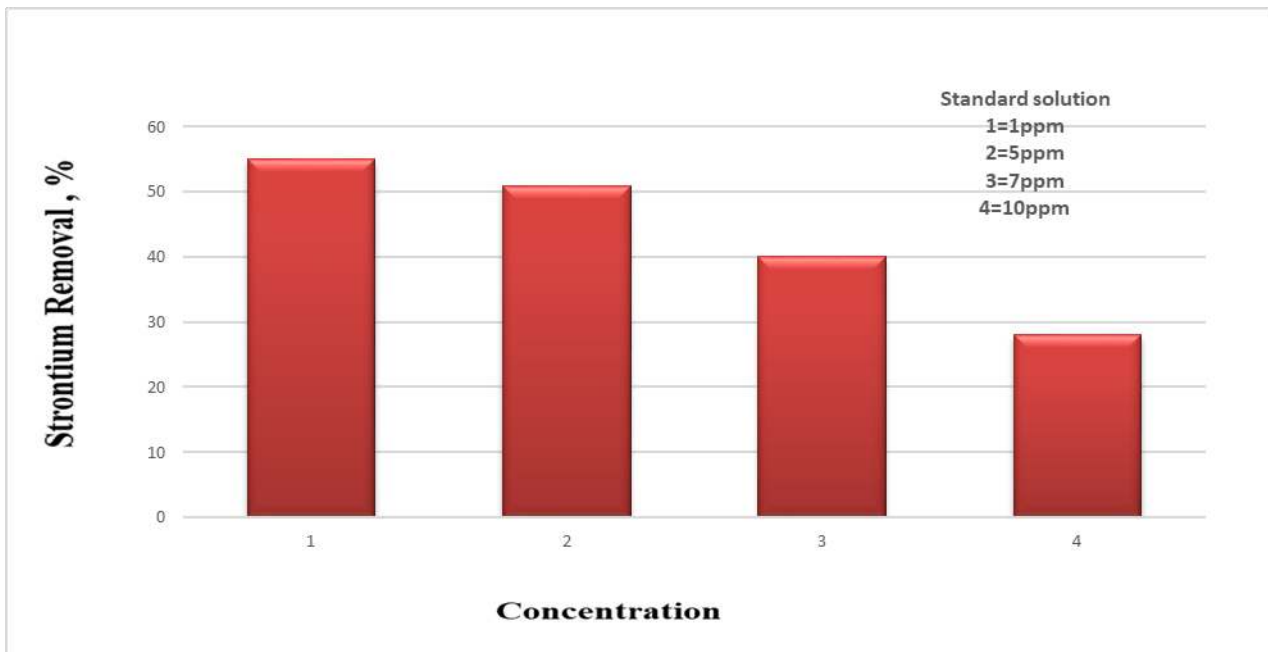


Figure 4. 7: Effect of Concentration on removing Strontium from synthetic solution at maximum removal

4.2.3 Effect of pH

The experiment carried out at different pH of medium showed that there was a change in the removal of boron and strontium over the different pH range shown in Fig4-8. At pH2 the adsorption efficiency was 30 % of boron and 25% strontium. When the increase pH 8 the adsorption efficiency first increased sharply and decreased less until pH 6.5. The maximum adsorption efficiency the boron at the pH 7, about 85% . The slight increase in adsorption efficiency of AC may be due to the more availability of free active sites of AC surface. It was found that the best absorption of boron is between 6-7 . (Bouguerra .et.al, 2008) .

The maximum strontium ion uptake was observed at the pH 6.5, and the adsorption efficiency reached about 53% . The slight increase in adsorption efficiency of AC may be due to the more availability of free active sites of AC surface. At low pH, the concentration of proton is high, so strontium ions binding sites become positively charged and then metal cations and protons compete for binding sites of adsorbent powder which results in lower uptake of strontium ions. As pH increases in the range from 2 to 6.5, the concentration proton exists in the solution will be decreased and hence will not give the chance to compete with strontium ions on the adsorption sites of the adsorbent powder, thus facilitating greater strontium ions uptake. After pH 7 the removal efficiency decreases as pH increases. It was found that the best absorption of strontium is between 6-7. (Hanafi, 2010).

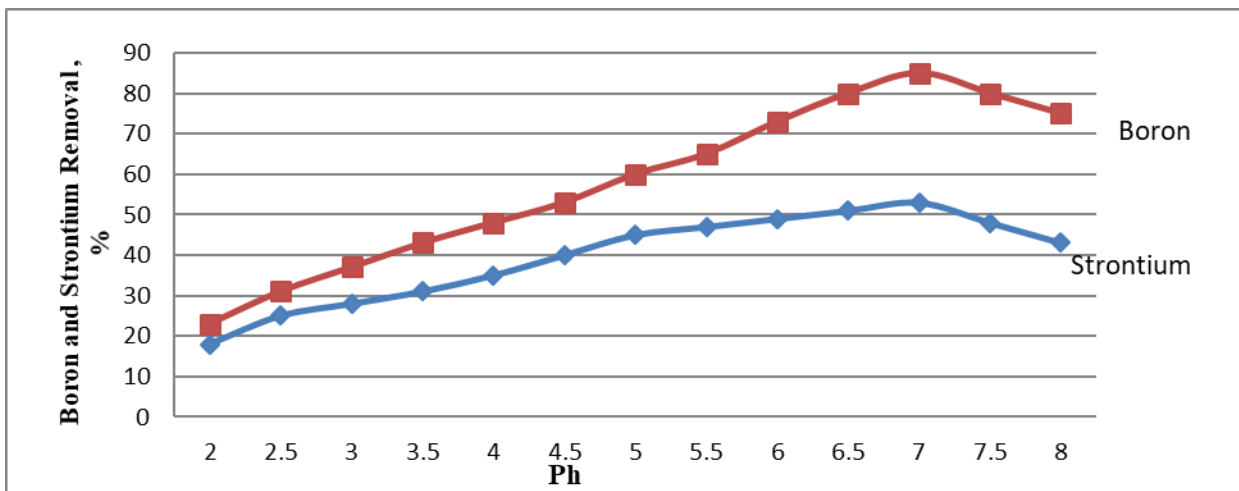


Figure 4. 8: Effect of pH on removing boron and Strontium from synthetic solution

4.2.4 Effect of temperature

In this section, the influence of temperature on the efficiency of boron and strontium removal is going to be discussed.

4.2.4.1 Effect of temperature on boron

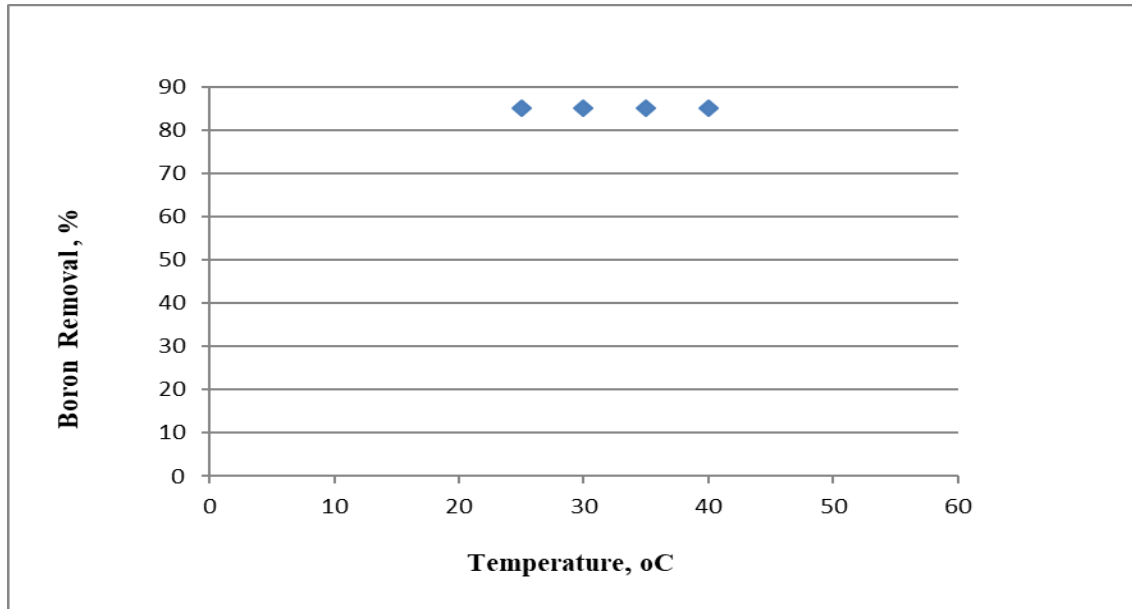


Figure 4. 9: Effect the temperature on removing boron

As can be seen from Fig. 4.9, an increase in temperature has no significant effects on the boron removal efficiency (Aksu .et.al, 2008).

4.2.4.2 Effect of Temperature on Strontium

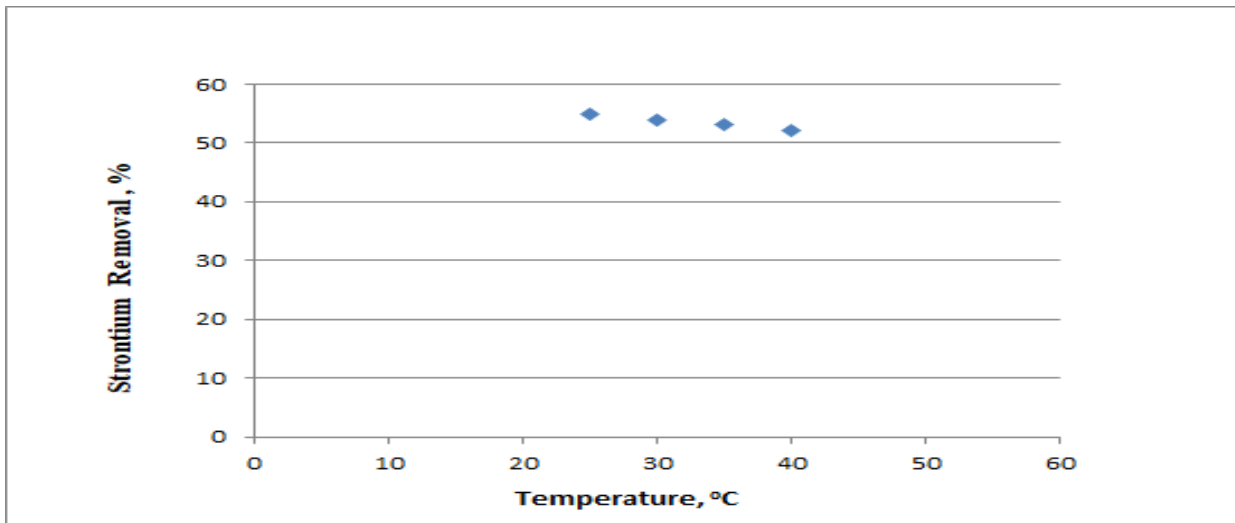


Figure 4. 10: Effect the temperature on removing Strontium

Figure 4-10 shows the effect of temperature of adsorption of Sr on the AC adsorbent. It is shown that the adsorption of Sr on AC e composite decreased as the solution temperature increased. This can be explained by the exothermic spontaneity of the adsorption process and by the weakening of bonds between Sr and active sites of adsorbents at high temperatures(Yusan et.al,2011) ,

4.3 Real water Samples from Wells efficiency in Boron and Strontium Removal

After the analysis of samples collected from water well, the results show that boron is 2.923 mg/l and Strontium is 11.205 mg/l and TDS 6200 mg/l. The following experiments have been done on a real water collected from Deir al-Balah from AL-Aqsa well. Figure 4-3 shows the initial concentration of boron and Strontium, the removed, and the residual concentration after 24 hours of adsorption by 1 gram of the produced activated carbon.

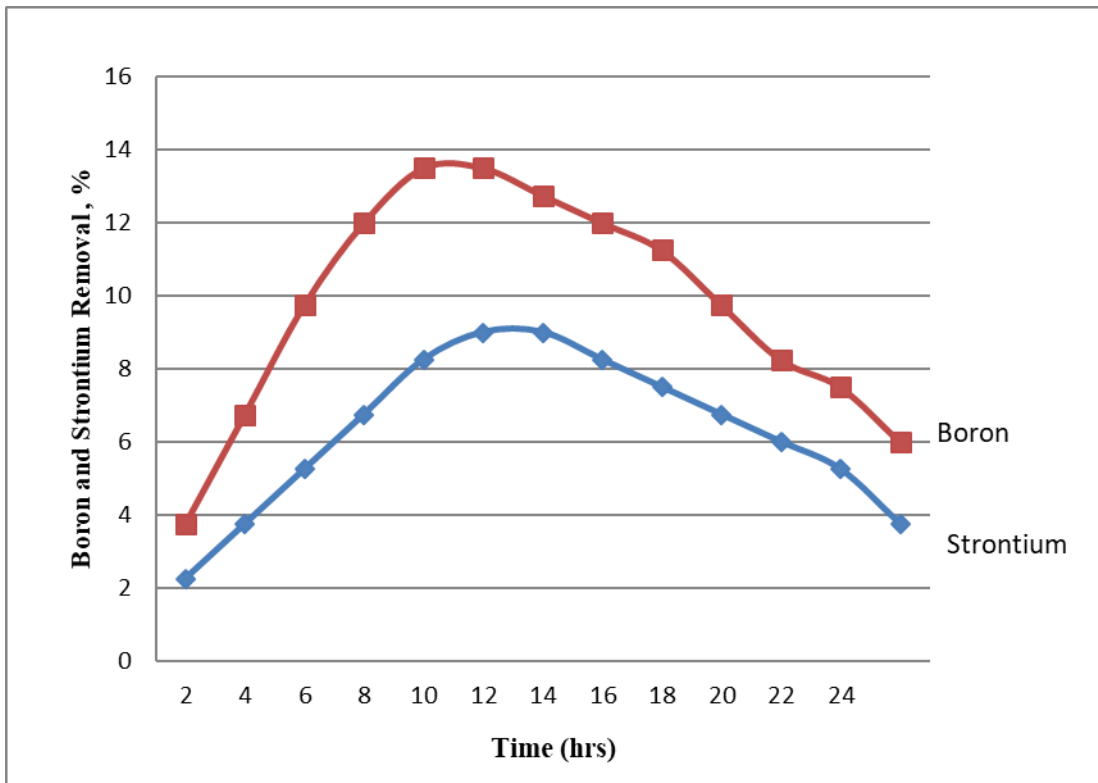


Figure 4. 11 Effect of water well Samples Removal boron and Strontium

Figure 4.11 shows the calculated percentage of the removal of the parameters, where the highest percentage recorded for the removal of the boron is 13.5% and for the removal of the Strontium is 9% . It's noticed that the percentage of boron and strontium removal in the water well is good due to total dissolved solid. This reduces the adsorption process or metals other than

boron and strontium disseverment . The more increased total dissolved solid, the more reduced removal boron and strontium .

4.4 Real Seawater Samples Efficiency in Boron and Strontium Removal

Analysis of samples collected from seawater beach well .the results show that boron is 4.5 mg/l and strontium 8.2mg/l . The following experiments have been done on a real seawater collected from Deir al-Balah desalination plant from beach well . Figure 4-12 show the initial concentration of boron and Strontium the removed and the residual concentration after 24 hours of adsorption by 1 gram of the produced activated carbon.

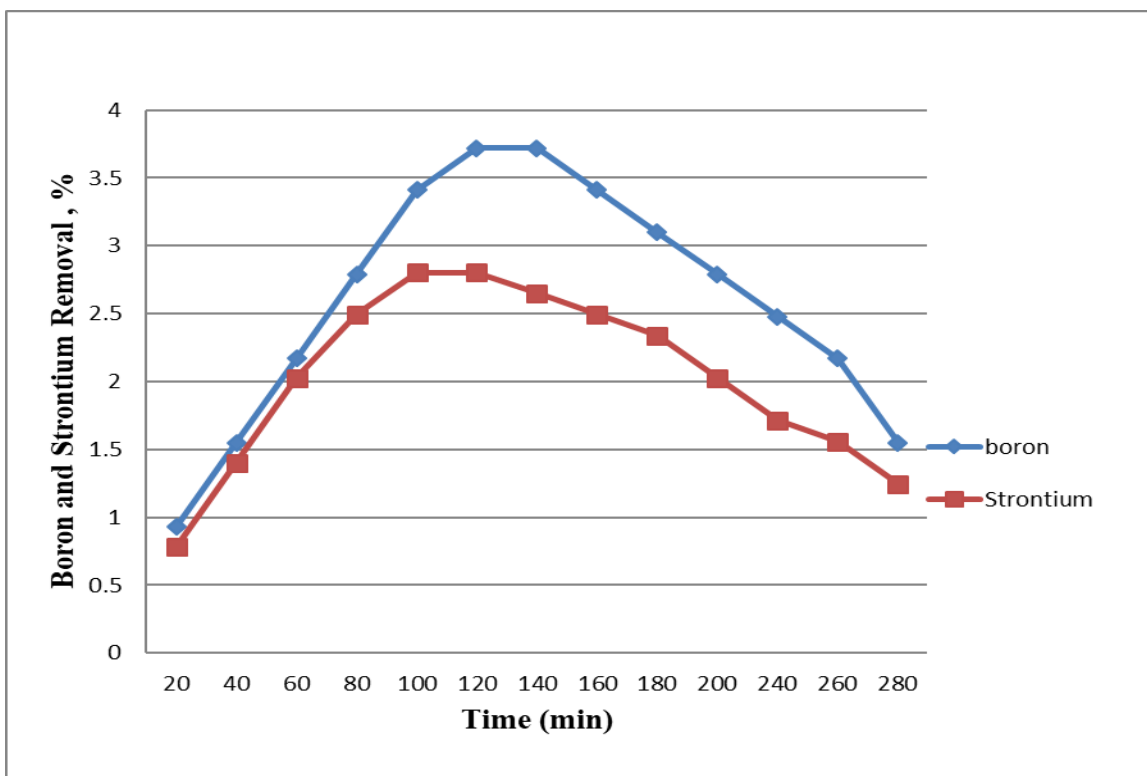


Figure 4. 12: Effect of seawater Samples Removal boron and Strontium

Figure 4-12 shows the calculated percentage of the removal of the parameters, where the highest percentage recorded for the removal of the boron is 3.7% and the removal of the Strontium is 2.8% . It's noticed that the percentage of boron and strontium removal in the sea water is low due to the very high percentage of total dissolved solid. This reduces the adsorption process or metals other than boron and strontium are dissolved.

CHAPTER FIVE
CONCLUSIONS AND
RECOMMENDATIONS

CONCLUSION

- Evaluating the potential of Olives Crushed Seeds as a precursor for activated carbon production was the main objective of the study. Another objective was estimating the adsorption capacity of the developed activated carbon for Boron and Strontium present in the sea water.
- We can produce activated carbon from crushed olive seeds under a carbonization temperature of 500°C and a constant flow of nitrogen 400 to 500 cm³/min. We can also activate it by heating with the assistance of KOH 1:2 w/w within 20 minutes .
- Adsorption has become an important method to remove heavy metal ions from water and wastewater. In this thesis, Preparation activated carbon from olives crushed seeds and applied to remove strontium and boron from aqueous solution. The result indicated that the adsorption equilibrium was reached at 12 h for boron and 6 h strontium . activated carbon beads may be a potential alternative absorbent for removing strontium and boron.
- Experimental data showed that boron and Strontium adsorption at pH value between 6 - 7.
- The process of treating olive seeds seems to be economical because olive seeds are mainly a waste material.
- This work contributes to the improvement of boron separation by sorption technique; it focuses on the Benefit waste material .
- The adsorption of strontium and boron on activated carbon beads is influenced by the pH and temperature and the boron concentration of the solutions.
- activated carbon is an effective adsorbent for the removal of strontium and boron.
- Low cost to produced activated carbon of this adsorbent with its adsorptive capability.
- Carbon activated by KOH was effective for strontium and boron removal more than the other adsorbents.

RECOMMENDATION

Some recommendation of this study are:

- Further testing of the Shells Activated Carbon before any future field-scale use of AC. Another recommendation is testing other agricultural waste material as a raw carbon source
- Further testing prior to future field-scale use of the Shell Activated Carbon is recommended to extend the observations and conclusions for other contaminants. In addition, testing for other available agricultural waste by products as a raw carbon source for activated carbon production because Olives Crushed Seeds will not be available throughout the year. Finally, field-testing of multiple organic impurities with actual source waters should be conducted because polluted waters may contain these organic impurities. This should be done to characterize the level of competition for available adsorption sites on the carbon and its effect on the operating life of the material.
- Studying the possibility of boron removal form wastewater treatment plants in order to use the treated wastewater for irrigation by Activated Carbon Produced from Olives Crushed Seeds .
- Studying and analyze the effect of the high concentrations of Boron and Strontium in the sources of irrigation water, coming from both water wells and wastewater reuse, and identify the capacity of different corps to resists boron effects.
- The legislating of the prevention and minimizing of importing the hygienic and chemical materials which includes high concentration of Boron and Strontium to reduce Boron and Strontium concentration in the waste water is highly recommended.
- More study on the economic feasibility of the activated carbon prepared from olive stones.
- Studying the adsorption efficiency of the prepared activated carbon on combined boron and Strontium solutions at the same time.
- More investigation on mode of action of KoH in carbon activation
- More study of boron and Strontium ion desorption from adsorbents.
- Further study other elements adsorption by using other types of AC.
- Further study on the economic feasibility of using the AC from olive stones.

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