

An-Najah National University

Faculty of Graduate Studies

**Phytochemical screening and adsorption of
Cu, and Ni ions from aqueous solution using
activated carbon from *Cupressus
sempervirens*, *Pinus halepensis* fruits**

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III

Dedication

This thesis is dedicated to:

My great parents; Mr. Ra'ed Ateeq and Mrs. Rehab Dwaikat.

My brother: We'am, sisters: Thara' and Karam

And my all friends

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Rawan Raed Ateeq

الإقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان :

**Phytochemical screening and adsorption of Cu, and Ni ions from
aqueous solution using activated carbon from *Cupressus Sempervirens*,
P.halepensis Fruits**

أقر بأن ما اشتملت عليه هذه الرسالة هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، و أن هذه الرسالة كاملة، أو أي جزء منها لم يقدم من قبل لنيل أي درجة أو لقب علمي أو بحثي لمؤسسة تعليمية أو بحثية أخرى.

Declaration

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

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Date:

التاريخ: 17/9/2017

Table of Contents

Dedication	III
Acknowledgement.....	IV
Declaration	V
Table of Contents	VI
List of Tables.....	IX
List of Figure.....	X
List of abbreviations.....	XI
Abstract	XII
Chapter 1	1
General Introduction	1
1.1 Heavy metals and techniques of removal:	1
1.1.1 Heavy metals introduction	1
1.1.2 Copper and Nickel impact in environment and human	2
1.1.3 Methods for heavy metals removal from waste water.....	4
1.2 Activated carbon and adsorption	6
1.2.1 Adsorption.....	6
1.2.2 Activated carbon	7
1.3 Antioxidant.....	9
1.3.1 Definition of antioxidant.....	9
1.3.2 Important of antioxidant in plant	9
1.3.3 Synthetic and natural antioxidants:.....	10
1.3.4 Trolox definition and structure:	11
1.4 Volatile oil.....	11
1.4.1 Volatile oil meaning:	11
1.4.2 Natural sources for volatile oil:.....	12
1.4.3 Characteristics and extraction methods for volatile oil:....	12
1.5 Cupressus sempervirens and P.halepensis fruits	13
1.5.1 Cupressus sempervirens classification and properties	13
1.5.2 P.halepensis description and properties	14
1.6 Objectives of this study.....	15
Chapter 2	17

VII

Materials and Methods	17
2.1 Materials and chemicals.....	17
2.2 Instrumentation	17
2.3 Collection and preparing plant materials	18
2.4 Methods and procedures:	19
2.4.1 Activated carbon preparation:.....	19
2.4.2 Experimental Set-Up for carbonization experiment.....	19
2.4.3 Carbon activation, yield, and removal efficiency:.....	19
2.4.4 Surface area measurement	22
2.4.5 Experiments of adsorption:	24
2.4.6 Preparation of volatile oil	27
2.4.7 Antioxidant activity	28
Chapter 3:	30
Results and Discussions	30
3.1 Iodine number surface areas	30
3.2 Percentage yield of prepared CFAC and PFAC samples	31
3.3 Scanning Electron Microscopic (SEM) and EDX for AC.....	31
3.4 Adsorption of Cu on AC from <i>Cupressus sempervirens</i> , <i>P.halepensis</i> , and Commercial AC.....	35
3.4.1 Effect of contact time:.....	35
3.4.2 Effect of adsorbent dosage:.....	37
3.4.3 Effect of pH:	37
3.4.4 Effect of Temp	38
3.4.5 Effect of concentration.....	39
3.5 Adsorption of Ni on AC from <i>Cupressus sempervirens</i> , <i>P.halepensis</i> , and Commercial	40
3.5.1 Effect of contact time.....	40
3.5.2 Effect of adsorbent dosage.....	41
3.5.3 Effect of pH.....	42
3.5.4 Effect of temp	43
3.5.5 Effect of concentration.....	44
3.5.6 Best parameters and max removal of Cu for different AC types	45
3.5.7 Best parameters and max removal of Ni for different A.C types	45

VIII

3.6 Adsorption isotherm on CFAC, and PFAC	46
3.6.1 Langmuir and Freundlich Isotherms for Cu	46
3.6.2 Langmuir and Freundlich Isotherms for Ni	48
3.7 Antioxidant activity	51
3.7.1 Antioxidant activity and IC ₅₀ for <i>Cupressus sempervirens</i> and Trolox.....	51
3.7.2 Antioxidant activity and IC ₅₀ for <i>P.halepensis</i> and Trolox	53
3.7.3 Percentage yield of <i>Cupressus sempervirens</i> volatile oil by ultrasonic microwave cooperative extractor/ reactor.....	55
Chapter 4	56
Conclusion and Recommendations	56
Conclusion:	56
Recommendation:	57
References	58
Appendix 1	67
Appendix 2	76
الملخص	ب

List of Tables

Table1: Speciation and Chemistry of Cu, Ni	3
Table 2: Heavy metals removal by <i>Cupressus sempervirens</i> or <i>P. halepensis</i> activated carbon:	5
Table 3: Cu, Ni removal by different activated carbon plants	7
Table 4: Instrumentations and Manufacturer	18
Table 5: Surface area of different AC according to iodine number test.	30
Table 6: Percentage yield of prepared activated carbon	31
Table 7: Best parameters and max removal of Cu for different A.C types	45
Table 8: Best parameters and max removal of Ni for different A.C	45
Table 9: Langmuir and Freundlich is isotherm model parameters and correlation coefficient of Cu adsorption onto: CFAC, PFAC and CAC	47
Table10: Langmuir and Freundlich is isotherm model parameters and correlation coefficient of Ni adsorption onto: CFAC, PFAC and CAC	49
Table 11: this work results vs. Nadeem Basalat results thesis.....	50
Table 12: Percentage inhibition activity for Trolox and <i>Cupressus</i> <i>sempervirens</i> in Palestine	51
Table13: IC ₅₀ value and equation of <i>Cupressus sempervirens</i> volatile oil in Palestine	52
Table14: Percentage inhibition activity for Trolox and <i>P.halepensis</i> in Palestine	53
Table15: IC ₅₀ value and equation of <i>P.halepensis</i> volatile oil in Palestine	54
Table 16: Percentage yield of <i>Cupressus sempervirens</i> volatile oil by ultrasonic microwave cooperative extractor/ reactor	55

Table1: Speciation and Chemistry of Cu, Ni.....	3
Table 2: Heavy metals removal by <i>Cupressus sempervirens</i> or <i>P. halepensis</i> activated carbon:.....	5
Table 3: Cu, Ni removal by different activated carbon plants.....	7
Table 4: Instrumentations and Manufacturer.....	18
Table 5: Surface area of different AC according to iodine number test.	29
Table 6: Percentage yield of prepared activated carbon.	30
Table 7: Best parameters and max removal of Cu for different A.C types	43
Table 8: Best parameters and max removal of Ni for different A.C	43
Table 9: Langmuir and Freundlich is isotherm model parameters and correlation coefficient of Cu adsorption onto: CFAC, PFAC and CAC.....	45
Table10: Langmuir and Freundlich is isotherm model parameters and correlation coefficient of Ni adsorption onto: CFAC, PFAC and CAC.....	47
Table 11: this work results vs. Nadeem Basalat results thesis.....	48
Table 12: Percentage inhibition activity for Trolox and <i>Cupressus sempervirens</i> in Palestine.....	49
Table13: IC ₅₀ value and equation of <i>Cupressus sempervirens</i> volatile oil in Palestine.....	50
Table14: Percentage inhibition activity for Trolox and <i>P.halepensis</i> in Palestine.....	51
Table15: IC ₅₀ value and equation of <i>P.halepensis</i> volatile oil in Palestine	52
Table 16: Percentage yield of <i>Cupressus sempervirens</i> volatile oil by ultrasonic microwave cooperative extractor/reactor.....	53

List of abbreviations

AC	Activated carbon
WHO	World Health Organization
EPA	Environmental Protection Agency
UCEPA	United States Environmental Protection Agency
MCL	Maximum Contaminant Levels
Ppm	Units are in milligrams per liter (mg/L)
CAC	Commercial activated carbon
CFAC	<i>Cupressus sempervirens</i> fruits activated carbon
PFAC	<i>P.halepensis</i> fruits activated carbon
<i>P.halepensis</i>	<i>Pinus halepensis</i>
DPPH	2,2- diphenyl- 1- by cryl- hydrazyl- hydrate
IC ₅₀	Half maximal inhibitory concentration
Λ_{\max}	Maximum wave length of absorption
SEM	Scanning electron microscopy
AAS	Atomic absorption spectroscopy
EDX	Energy- dispersive X- ray spectroscopy
Trolox	6-hydroxy- 2,5,7,8- tetramethylchroman-2- carboxylic acid
JUST	Jordan University of Science and Technology/ Nanotechnology Institute
PNP	P- nitro phenol

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Abstract

Background: Heavy metal ions have become hazard and toxic in environment, due to their accumulation in living organisms. Copper and nickel pollution raised from copper mining and smelting, brass manufactures, electroplating industries and excessive use in agri-chemicals. High concentration of nickel and copper causes chronic and acute diseases such as cancer of lungs, nose and bone. Many different techniques are available for removing heavy metal from aqueous solution, the most effective and inexpensive method is activated carbon that used in this study.

Objectives: The current investigation aimed to remove copper and nickel ions from aqueous solution by adsorption activated carbon, as adsorbent prepared from *Cupressus sempervirens* and *Pinus halepensis* fruits using different activated agent. This study also aimed to determine the antioxidant test for volatile oil from *Cupressus sempervirens* and *Pinus halepensis*.

Methods: The samples of *Cupressus sempervirens* and *Pinus halepensis* fruits were collected from different areas of Palestine. Physical and chemical activating was studied in adsorption experiments; it was conducted at different parameters such as: concentration, pH, time, dosage and

temperature. Different activated agent also studied to determine the maximum surface area for *Cupressus sempervirens* and *Pinus halepensis* fruits. SEM, EDX and iodine number tests were studied to support the results. Antioxidant capacity was estimated by using DPPH assay and UV-spectrophotometric method. In addition percentage yield of *Cupressus sempervirens* volatile oil was determined using ultrasonic microwave cooperative extractor/ reactor.

Results: The obtained results showed that the activated carbon produced from *Cupressus sempervirens* and *Pinus halepensis* fruits give good percentage yields which reach up 40% and 68%, respectively. Optimum percent of Cu removal was 99.9% when *Cupressus sempervirens* fruit activated carbon (dosage 0.2g, at pH=12) is used while Ni removal was 99.6 % (dosage 0.2g, at pH=2). Optimum percent of removal was 99.1% when *Pinus halepensis* fruit activated carbon (dosage 0.2g, at pH=4) is used, while Ni removal was 98.5% (dosage 0.2g. at pH=7). The results showed that equilibrium time of Cu, Ni adsorption on CFAC and PFAC is 24 hours. The optimum temperature for *Cupressus sempervirens* and *Pinus halepensis* was 25°C.

Surface area determined by iodine number showed 726m²/g for *Cupressus sempervirens* using H₃PO₄ (phosphoric acid) as activated agent and 1257.3 m²/g using NaHCO₃ (Sodium bicarbonate) for *Pinus halepensis*, the SEM-EDX analysis showed the same results. Adsorption isotherms were studied at 25°C, Freundlich isotherm was fitted for *Cupressus sempervirens* and *Pinus halepensis*.

On the other hand, antioxidant activity showed different results in different areas in Palestine. The IC_{50} of the antioxidant *Cupressus sempervirens* in Palestine can be ranked: south Palestine>north Palestine>middle Palestine, and for *Pinus halepensis*: north Palestine>middle Palestine>south Palestine, by using Trolox as a reference.

Conclusion: Results of this study show that both of *Cupressus sempervirens* and *Pinus halepensis* may be useful for the development of method for removal of different heavy metals in different parts of these plants also it can be used as alternative to the commercial activated carbon.

Chapter 1

General Introduction

1.1 Heavy metals and techniques of removal:

1.1.1 Heavy metals introduction

"Heavy metals" pretend a risk to public health due to their toxic, carcinogenic and accumulation, non-biodegradable nature, and widespread in human and natural environment. They are natural components of the earth's crust, which have atomic number >20 and atomic density greater than 4000 kg/m^3 , or more than water 5 times [1, 2].

Heavy metals are very toxic and poisonous at low conc., although some are essential for metabolic activity in living organisms at low conc. like Cu, Fe, other metals like Pb, Cd are non-essential, at high concentration they can fetal living organisms [1-3]. They introduced into the environment from metal plating, battery, mining, petroleum and paper industries, pesticides and fertilizers [3, 4].

Heavy metals are not biodegradable and accumulate in living organisms causing chronic and acute diseases. The toxicity, mobility and reactivity of heavy metals depend on its speciation, and some condition. e.g.: pH, temp, solubility and time contact [2, 5].

1.1.2 Copper and Nickel impact in environment and human

Copper (Cu)

Copper is a transition metal that is stable in its metallic state and forms monovalent (cuprous) and divalent (cupric) cation. Dissolved copper can impart blue-green or light-blue color [6].

Copper pollution has very hazard and toxic in the environment and mammalian, the source of copper pollution in ground water is from copper smelting, mining, electroplating, and petroleum industries, the sources of contaminant in drinking water is corrosion of house hold plumbing system; erosion of natural deposits. Potential health from long term exposure of Cu above the MCL (unless specified as short term) is liver or kidney damage, and in short term Gastrointestinal distress.

People with Wilson's disease should consult their personal doctors the amount of copper in their water exceeds the action level. WHO exhort the max acceptable Cu conc. in drinking water must be less than 3000 ppm [6, 7].

Nickel (Ni)

Nickel (density: 8.9 g/cm³, atomic number: 28, atomic weight 58.69) is silver in color, magnetic, hard and malleable, it conducts electricity. Compounds of nickel are green in color. Pure nickel metal is used to prepare nickel alloys (including steel) [8-10].

Nickel is widely used heavy metal in different industries, it is found in electroplating, battery, silver cleaner. Nickel is a toxic heavy metal due to cause chronic toxicity to environment and humans, ingested Ni (as soluble Ni compounds) cause decreased body and liver weight, cellular degeneration

in kidneys and liver, damage the immunes system. So removing nickel (II) from industrial waste water before discharged is important [11].

In 1987, the EPA established an oral reference dose (acceptable daily intake) for Ni of (20 μ g/Kg/day), the MCL for this element in drinking water was 100 μ g/L assuming 70 Kg adults drinks 2L/day [8, 9, 11].

Table (1) showed the speciation and chemistry of Cu, Ni found at contaminated sites [2, 8].

Table1: Speciation and Chemistry of Cu, Ni

Heavy Metal	Speciation and Chemistry	Conc. limits	References
Copper	Cu occurs in 0, +1, +2 oxidation states. The most toxic species of Cu is cupric ion (Cu^{2+}), e.g: $\text{Cu}_2(\text{OH})_2^{+2}$. CuCO_3 is the famous soluble species in aerobic alkaline system, but in anaerobic environments ($\text{CuS}_{(s)}$) will form in presence of sulphur. Copper forms strong solution complexes with humic acid	Conc. in natural soil: 2-100 ppm. Plants natural range: 5-30ppm. Toxicity level in plant: 30-100ppm. USEPA MCL in water : 1.3 ppm	Dzombakand Morel, 1990 [12]. LaGrega et al., 1994 [13].
Nickel	Ni occurs in +2, +3, +4; it is stable in aqueous solution in the +2. Slowly attacked by dilute HCl, H_2SO_4 and is readily attacked by nitric acid. Fused alkali hydroxides do not attack Ni. Nickel salts e.g.: chloride acetate, nitrate are water soluble. Ni mostly as the ion $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ in natural waters at pH 5–9	USEPA MCL in water : 100 ppm Smoke one cigarette contains about 0.04–0.58 μ g of nickel. Ni levels in food are generally in the range 0.01–0.1 ppm	Tundermann et al., 2005 [14]. Kerfoot, 2002 [15]. WHO (2005) [16].

1.1.3 Methods for heavy metals removal from waste water

Many methods have been developed for heavy metals removals from water, the most common process for heavy metals removal from contaminated water include precipitation, ion- exchange, reverse osmosis, activated carbon adsorption, oxidation- reduction, biological process, and electro-coagulation. The most of these methods are high cost and not easy to operate. e.g.: ion- exchange and reverse osmosis. Different methods of removal of heavy metals by *Cupressus sempervirens* and *P.halepensis* A.C showed in table (2) [3, 4, 17, 18].

Table 2: Heavy metals removal by *Cupressus sempervirens* or *P. halepensis* activated carbon:

Cupressus sempervirens of P.halepensis	Heavy metals removal	% removal or capacity	Methods	References
<i>Cupressus sempervirens</i> , <i>P.halepensis</i> leaves	Pb	<i>P.halepensis</i> > <i>Cupressus sempervirens</i>	Decaying plant leaves	M.M. Al-Subu (2001)[19].
<i>Cupressus sempervirens</i> leaves	Ni	Max removal at pH= 8.5 for <i>Cupressus sempervirens</i> and pH= 6.7 for <i>P.halepensis</i>	Decaying plant leaves	R.Salim (1988) [20].
<i>Cupressus sempervirens</i> and <i>P.halepensis</i>	Cd	In acidic solution: <i>Cupressus sempervirens</i> > <i>P.halepensis</i> In neutral solutions: <i>P.halepensis</i> > <i>Cupressus sempervirens</i> .	Soaking plant leaves	Oraib Sayrafi, Radi Salim (1999) [21].
<i>P.halepensis</i> Sawdust	Cu^{2+} , Pb^{2+} , and Cd^{2+}	$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$	Adsorption by sawdust	Yanbo Zhou. Et al. (2015) [22].
crushed <i>P.halepensis</i> needles	Ni and Cd	The highest metal removals at high pH	Activated Carbon	A. Damaj, et al. (2015) [23].

1.2 Activated carbon and adsorption

1.2.1 Adsorption

1.2.1.1 Adsorption definition and process

Adsorption is the mechanism which included the transfer of a material from a solution onto the surface of solid adsorbents by chemical or physical attraction. Physical adsorption contains attraction by electrical charge differences between the adsorbent and the adsorbate. Chemical adsorption is the action between the adsorbent outside and the adsorbate [24, 25].

Adsorption includes transport of the soluble materials to the surface of the fixed adsorbent, where the adsorbate then moves into the adsorbent pores [26].

1.2.1.2 Adsorption face

Adsorption has been found to be better than other approaches for water cleaning in title of: cost, simple of application, ease of design and operation, does not need high skilled maintenance [27].

1.2.1.3 Adsorbents used to remove Cu and Ni from aqueous solution:

Research workers used many different low-cost adsorbents from crop wastes like: coconut coir pith [28], rice husk [29], peanut hull carbon, almond shell carbon, hazelnut shell [30, 31], almond husk and tea leaf [11] for the removal of copper and nickel from water and contaminated water. Table (3) showed the Cu, Ni removal by different plant AC.

Table 3: Cu, Ni removal by different activated carbon plants

Modified material(plants)	Metals removal (Cu, Ni)	References
Oil Palm Coconut shells	Ni	Noklesur M.Rahman, Mohd Adil. Et al., (2014). [32]
Almond Husk	Ni	Halil Hasar (2003). [11]
Hazelnut shell	Cu	E.Demirbas, N.Dizge, et al., (2009). [33]
Asphodelus Ramosus tuber	Cu	Mahameed. A. (2017)[34]

1.2.2 Activated carbon

1.2.2.1 Properties of activated carbon

Different techniques and processes used to remove the pollutants from polluted water; adsorption is one of the most common techniques, efficient, effective, and low cost methods for water cleaning. The adsorbents involve activated carbon surface reactivity, high surface area, and porous structure, highly inert and thermally stable, used in a broad pH range, and easily increase adsorption capacity by use different chemical treatment; these features make activated carbon the most common and abroad used adsorbent in water cleaning [35].

1.2.2.2 Activated carbon efficiency

AC efficiency for removing a given pollutant depends on both its adsorption capacity and surface chemistry. The AC adsorption capacity is usually referring to its internal pore volume that may be scattered throughout the solid as pores range in width from micro pores to macro pores [36].

When the sizes of pore of the activated carbon are in the size range of the pollutants, adsorption mechanism will be boost and is expected to be capable. Adsorption capacity of the finished AC depends on the structural properties of the original precursor material and on the type of the activation technique [37].

There are two different methods used to get carbon with good adsorption by developing excellent surface characteristic and specific functionalities. The main two methods for of activated carbons preparation are: physical and chemical activations [38].

1.2.2.3 Physical activation:

The physical activation method includes carbonization of adsorbents and following activation at high temperature (400-1000) in a carbon dioxide or steam atmosphere [39] or using N₂ gas as carbon gaseous activating agent [40].

1.2.2.4 Chemical activation and activation agents:

The chemical activation process involves raw material carbonization previously saturated with a chemical agent such as KOH, ZnCl₂, NaOH, NaHCO₃ etc. The features of chemical activation over physical activation can be performed at low temperature, and get higher yield than the physical activation [41].

1.3 Antioxidant

1.3.1 Definition of antioxidant

The “antioxidant” word is increasingly famous in modern society. The definition of antioxidant in dictionary is "a substance that opposes oxidation or inhibits reactions promoted by oxygen or peroxides, many of these substances used as preservatives in various products (as in oils, food products, and in fats)” [42]. Antioxidants refer to compounds that reduce autoxidation of a chemical product such as plastic and rubber in the chemical industry [43]. In medicine and biochemistry, antioxidants are enzymes or other organic substances, such as β -carotene or vitamin E that are suitable facing the effects of oxidation in tissues of animal [44]. In food science, antioxidants have a broader meaning, as defined by the Institute of Medicine: they include components that prohibit fats in food from becoming rancid as well as dietary antioxidants “a substance in foods that significantly decreases the unfavorable effects of reactive species, such as reactive nitrogen and oxygen species, on normal physiological function in humans” [45].

1.3.2 Important of antioxidant in plant

In recent years, increasing attention has been paid by consumers to the health and nutritional aspects (mineral elements, vitamins contents, and antioxidants, etc.) of horticultural products. A diet contains vegetables and fruits protection against some common diseases such as cancer and cardiovascular events [46].

The importance of the antioxidant, flavonoids and other phenolic, constituents of plant materials enhanced health and protection from cardiovascular disease and cancer is also raising interest among scientists, food manufacturers, and consumers as the trend of the future is moving toward functional food with specific health effects [47].

1.3.3 Synthetic and natural antioxidants:

The antioxidants are divided into two basic groups; natural and synthetic. Compounds with structures of phenolic indifferent degrees of alkyl substitution are called synthetic antioxidants. These compounds such as butylated hydroxyl toluene (BHT) and butylated hydroxyanisole (BHA) have been used as antioxidants since the beginning of past century. The synthetic antioxidants are restricted to use, because they are carcinogenic materials [48].

On the other hand, natural antioxidants can be; nitrogen compounds (i.e. amino acids), phenolic compounds (i.e. flavonoids), or carotenoids (i.e. ascorbic acid).

Many of these antioxidants, like flavonoids, have biological effects in a wide range they include; antiviral, antibacterial, ant allergic, and cardiovascular treatment, so the concern of natural antioxidants has increased in last years because they important for life [48].

1.3.4 Trolox definition and structure:

Trolox (6-hydroxy- 2,5,7,8- tetramethylchroman-2- carboxylic acid), has chemical formula $C_{14}H_{18}O_4$, and molar mass- 250.29 g/mol. Trolox is soluble in water, it is an antioxidant like vitamin E. Trolox is used in different applications biological or biochemical to reduce oxidative stress or damage. In this research Trolox use as a reference [49].

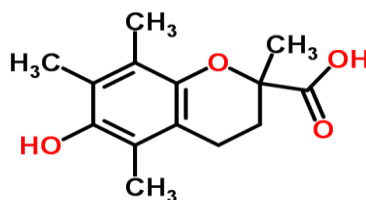


Fig.1: Trolox Structure

1.4 Volatile oil

1.4.1 Volatile oil meaning:

The definition of volatile oil in dictionary is "oil that evaporates easily; such oils occur in aromatic flora, to which they give flavor and other characteristics." In Herbal medicine volatile oil meaning: "A general word of essential oil of plant origin which volatilizes (i.e., is aromatic: limonene, thymol). On the other hand, Medical Dictionary for the Health Professions and Nursing define volatile oil as "A substance of oily feel and texture, derived from a plant and involves the principles to which the taste and odor of the plant are due (essential oil); in opposite to a volatile oil, a fatty oil

evaporates when exposed to the air and able of distillation the synonym(s) is: ethereal oil [50, 51, 52].

1.4.2 Natural sources for volatile oil:

In the last years, there has been growing concern in naturally phytochemical compounds with anti-cancer probable, because they are relatively: cheap, nontoxic, and available. More than 25% of drugs used during the last 2 decades are directly derivative from plants, although the other 75% are chemically modified by natural products. Volatile oil can be produced by all parts of plant, includes: stems flowers, twigs, buds, seeds, fruits, leaves, roots, wood or bark, and are reserved in cavities, secretory cells, glandular trichomes or epidermic cells [53, 54, 55].

1.4.3 Characteristics and extraction methods for volatile oil:

Volatile oils are important in the plant by plant protection of; fungi, virus, bacteria and insecticides. They also attract some insects to transport pollens and seeds by its favour [56, 57].

Volatile oils are used by Arabs in several centuries ago; they are used in locally anesthetic remedies, antiseptic, foods preservation, embalmment, sedative, and as antimicrobial. Until now, these uses haven't changed except that known more about action mechanisms, especially in antimicrobial level [56].

There are different methods for extracting volatile oils. These include: microwaves, liquid carbon dioxide, and distillation using hot steam or boiling water in different pressure. The yield of extraction can vary in method

type of extraction, quantity, quality, and content of soil, climate, time of harvest, and area of plant. So to get volatile oils of constant content, the extraction will be under the same setting method of extraction and same condition of the plant: same soil, same source, and same season [57, 58, and 59].

1.5 Cupressus sempervirens and P.halepensis fruits

1.5.1 *Cupressus sempervirens* classification and properties

Cupressus sempervirens refer to coniferous trees which evolve also pin, and fir. Conifers fit to growth in many areas around the world. Some are the Earth's greatest plant and many species of *Cupressus* adapt to growth around the world which is different with tall, size, shape, and fruits [60].

Tree 10-30 meter, with stem up to 1 meter in diameter. Branches very heavy, horizontally or straight up spreading, small branch more or less in 2 rows. Leaves imbricated and crossed, triangular, and convex. 2-3 cm of ovulate complete cones. Seeds 5-7 mm. furnished with a small wing, ripening 1 year after pollination. Yields tannins and timber; oil derived from leaves was used in medicine and perfumery [61].

Cupressus sempervirens of Mediterranean fruits activated carbons are one of aims of this study to use for water purification. *Cupressus sempervirens* is the scientific name of Mediterranean *Cupressus Sempervirens*. *Sempervirens* is the species name comes from the Latin for 'evergreen'. It has other names like as Italian *Cupressus sempervirens* depending on this region, and "drama tree" because of its tendency to bend with even the least of air [62].

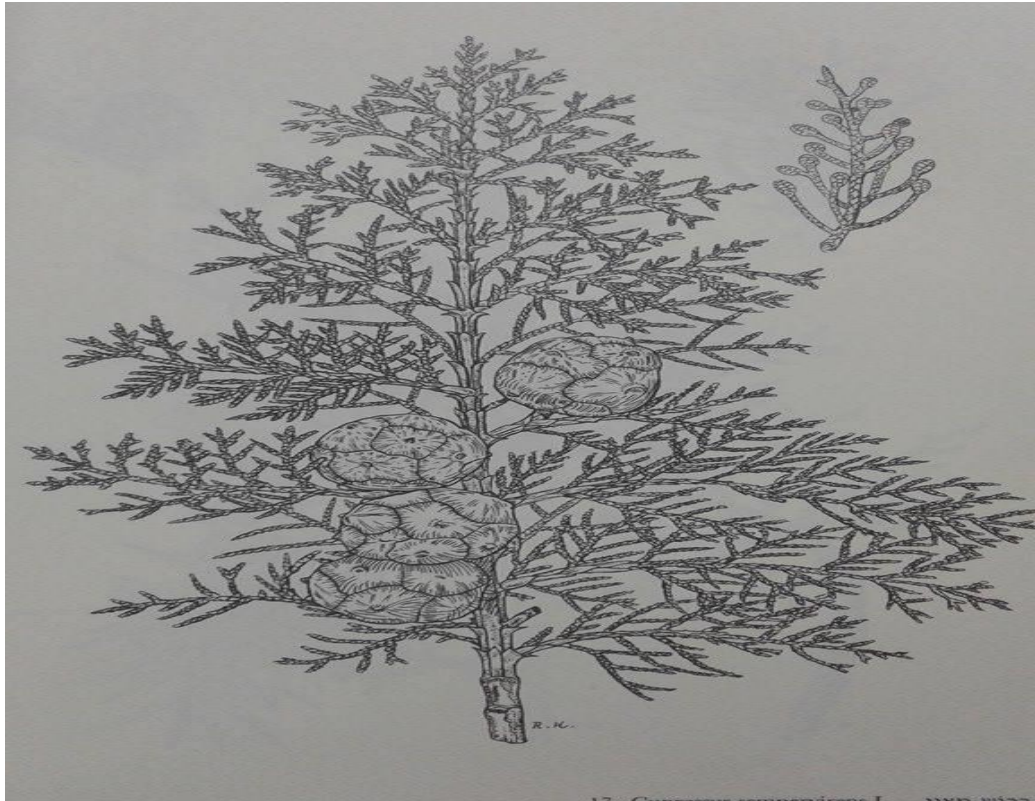


Figure (2): Cupressus Sempervirens

1.5.2 *P.halepensis* description and properties

Area: Mediterranean, tree 6-15 meter, with distributed crown and ascending somewhat whorled branches. Leaves in pair's 8-15 cm bright green. Staminate cones clustered in heads, ovoid to cylindrical. Seeds 5-6 x 3 mm. Mature cones 7-12x4-6 cm. solitary or 2-3 in a whorl, reflexed on thick peduncles, oblong or oblong- conical, reddish- brown, exposed portion shining, flat, rhombic, transversely keeled, with small flattish umbo, wing 3-5 times as long as seed, maturing 15-16 months after pollination Seed maturing July- August [63].

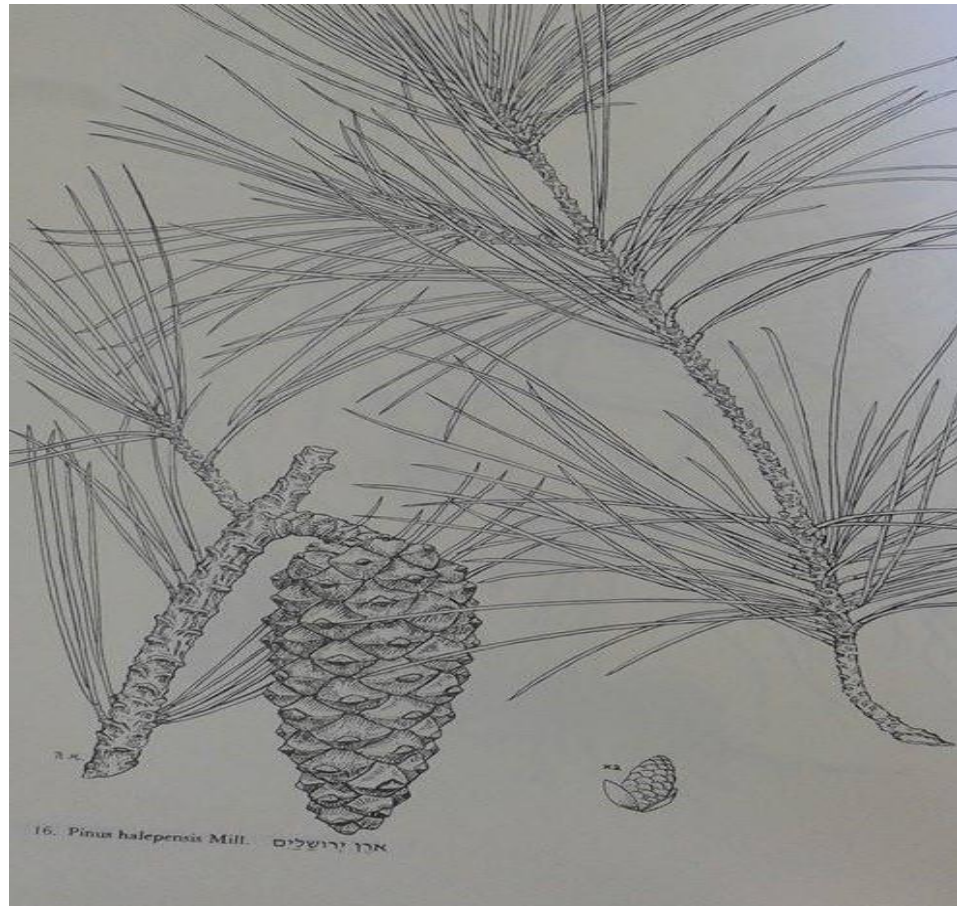


Figure (3): Pinus halepensis

1.6 Objectives of this study

The main objectives of this research are the following:

- Finding a good method for carbonization of *Cupressus sempervirens* and *P.halepensis* fruits
- To develop a low cost high-grade activated carbon from *Cupressus sempervirens* and *P.halepensis* fruits.
- Temperature, pH, Conc., dosage and time effects will be studied also on adsorption of contaminant.

- Using activated carbon for heavy metals removal from contaminated water.
- To compare the characteristics of commercial activated carbon and *Cupressus sempervirens* and *P.halepensis* fruits derived activated carbons for heavy metal adsorption from aqueous solution.
- Studying the antioxidant test for volatile oil from two plants.

Chapter 2

Materials and Methods

2.1 Materials and chemicals

All the used chemicals were of analytical grade. H_3PO_4 (85%), NaOH, were purchased from Frutarom. NaHCO_3 , $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$ and activated charcoal were purchased from Sigma-Aldrich. ZnCl_2 was purchased from Chem-Samuel. HCl was purchased from Merck. Methanol was purchased from Lobachemie. DPPH (2, 2-Diphenyl-1-picrylhydrazyl), and Trolox (6-hydroxy- 2, 5, 7, 8 -tetramethychroman-2 carboxylic acid) were purchased from Sigma-Aldrich.

2.2 Instrumentation

All the instrumentations that used in this study were from Faculty of Science and Pharmacy Departments at An-Najah National University except SEM tests instrumentations which were conducted at Jordan University of Science and Technology/Nano Institute in Jordan.

All glassware's were used: volumetric flasks (10ml, 50ml, 100ml,) Round-bottom flasks (1000ml), glass rod, graduated cylinders (10ml, 50ml), separator funnels and beakers (100ml, 250ml, and 1000ml). All used instrumentations presented in Table 4.

Table 4: Instrumentations and Manufacturer

No.	Instrumentations	Manufacturer
1.	Grinder	Polinex model, Uno.- China
2.	Balance	Radwag, AS 220/c/2- Poland
3.	Micropipettes	Finn pipette- Finland
4.	Incubator	Nuve- Turkey
5.	Shaker	Memmert Shaking Incubator- Germany
6.	Hot plate stirrer	Daihan Labtech- India
7.	Spectrophotometer	Jenway 7135- England
8.	Heavy duty tubular regulated furnace	Lindberg 9001-
9.	pH-meter	Jenway -3510.
10.	Microscope	Emission Scanning Electron Microscopy (JUST/Nanotechnology Institute)2017
11.	Ultrasonic Microwave Cooperative Extractor\ Reactor	Model: MW-ER-01 Serial number: UM2015042801A

2.3 Collection and preparing plant materials

In this work, *Cupressus sempervirens* and *P.halepensis* fruits were collected from different cities in Palestine (north, middle and south). They were used as raw material for the production of activated carbon in different procedures and extracted volatile oil. The samples were collected in (December 2016) and stored in chemical lab at faculty of science at An- Najah University, until they were used.

2.4 Methods and procedures:

2.4.1 Activated carbon preparation:

The activating agent and the general procedures of carbonization and activation in this research were chosen from prior works [37, 39, and 61] with some modification.

2.4.2 Experimental Set-Up for carbonization experiment

Heavy duty tubular regulated furnace Lindberg 9001 was used to carbonize *Cupressus sempervirens* and *P.halepensis* fruits separately. Each sample (weight =50g) was inserted into the furnace in a (0.04 m inner diameter and 0.74 m length) and 0.25 cm thick stainless steel tubes. The furnace was heated to get carbonization temperature (450°C) at a heating rate increase (20°C/min). The sample was kept at the temperature for 50 min, under inert atmosphere (99.9% N₂ gas) at (0.5 L /min) flow rate. Then, the activated carbon was cooled, and a yield was recorded.

2.4.3 Carbon activation, yield, and removal efficiency:

Different processes were used to prepare activated carbon at the same temp (450 °C) and the same time (50 min) in the tube furnace, the name of AC sample, activation methods, and yield of *Cupressus sempervirens* and *P.halepensis* are given in Table 2. The yield of the AC was calculated from the following equation:

$$\text{Yield of AC (wt\%)} = \frac{\text{weight of activated carbon}}{\text{weight of cypressorpine fruits}} * 100 \quad (2.1)$$

2.4.3.1 Cu, Ni removal efficiency:

Adsorption efficiency of Cu, Ni was calculated by using the following equation:

$$\% \text{ removal efficiency (Cu or Ni)} = \frac{C_i - C_f}{C_i} * 100 \quad (2.2)$$

Where C_i : initial concentration of heavy metal, C_f : is the final or residual concentration of Cu or Ni by AAS reading in mg/L [64].

2.4.3.2 Physical activation:

Cupressus sempervirens and *P.halepensis* samples were carbonized at 450°C for 50 min without addition of any chemical. After cooling, the two samples were washed with deionized water to remove dust, and then dried in an oven at 110°C, then grinding by blender to get a fine powder. Finally, they were stored for further use. These samples were named as (CFAC, PFAC) for *Cupressus sempervirens* and *P.halepensis* respectively.

2.4.3.3 Chemical activation:

To prepare AC from *Cupressus sempervirens* and *P.halepensis* fruits, different chemical reagents were used: $ZnCl_2$, NaOH, $NaHCO_3$, and H_3PO_4 . The samples were then carbonized.

2.4.3.3.1 Carbon activation by zinc chloride:

Each sample of *Cupressus sempervirens* and *P.halepensis* fruit (50g) was mixed with zinc chloride solution (200 mL, 20 % w/w) by stirring.

In this work, impregnation with zinc chloride was carried out at 80°C in a water bath 2 hr. Then, 2 samples were washed with deionized water and filtered, then dried at 100°C in an oven. After that, they were carbonized at 450°C for 50 min. The carbonized product was washed with 0.50 M (HCl) solution and with deionized water in order to remove the residual activating agent. The final product was dried in an oven at 100°C and stored for use. These samples were named as (CFAC/ZnCl₂, PFAC/ZnCl₂) for *Cupressus sempervirens* and *P.halepensis* respectively.

2.4.3.2.2 Carbon activation by phosphoric acid

60g of *Cupressus sempervirens* or *P.halepensis* fruits was added to the phosphoric acid solution (200 mL, 50% w/w) and stirred at 90°C for 2 h. After this impregnation process, the solution was filtered and washed with deionized water, dried in an oven at 100°C, before carbonization at 450°C for 50 min. After that, the product was washed with hot, cooled deionized water respectively to get neutral pH of the filtrate. The AC was then dried in an oven at 100°C and stored for use. This sample was named (CFAC/H₃PO₄).

2.4.3.2.3 Carbon activation by sodium bicarbonate:

Two samples of *Cupressus sempervirens* and *P.halepensis* (30g each) were mixed with NaHCO₃ solution (300 mL, 10% (w/w)). The impregnation was

carried out at 50°C for 5 h. The samples were filtered and dried at 25°C. Sample carbonization was performed at 450°C for 50 min. Finally, the AC products were treated as ZnCl₂ activation and stored for used. These AC were named as CFAC/NaHCO₃ and PFAC/ NaHCO₃.

2.4.3.2.4 Carbon activation by sodium hydroxide

Each of 2 samples 30g *Cupressus sempervirens* and *P.halepensis* fruits were mixed with NaOH at a ratio (1: 0.5) w/w. This mixture is placed in 1000 ml round bottom flask, where distilled water is added (600 ml). The solution is refluxed for 2 hr. at 70 °C, cool and then decanted. Then dried in the oven at 100°C. These samples are carbonized and activated for 50 min under 450 °C. These AC were named as CFAC/NaOH and PFAC/ NaOH.

2.4.4 Surface area measurement

The adsorption capacity of AC is affected by different parameters, surface area and porous structure [65]. In this research, the surface area of the final AC was measured using the method of Iodine Value and Scanning Electron Microscopy (SEM).

2.4.4.1 Iodine number

Iodine number indicates of (0 – 20 Å) micro pore content, the procedure and reagents used in the iodine test are in the following:

Prepare 0.1N of iodine solution by dissolving (12.7 g iodine and 19.1g of (KI)) in 1 Liter of deionized water. In another volumetric flask 0.05N of

sodium thiosulphate pentahydrate solution (12.5 gm $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 1 liter deionized water) was prepared. Starch solution freshly prepared 1%.

Iodine solution standardization

In conical flask (10 ml / 0.1N) of Iodine solution was taken, titration with 0.05 N Sodium thiosulphate to get a pale yellow, and then added 3 drops of starch solution (1%), the color turned blue, continue titration to get a colorless solution; burette reading is blank reading (B).

Test of activated carbon:

0.2 gm of activated carbon (*Cupressus sempervirens*, *P.halepensis*) was put into flask, then 40 ml of iodine solution was added (0.1 N), shaken for 5 minutes and filtered, 10 ml of the filtrate was titrated with sodium thiosulphate solution using 1% starch as indicator, this burette reading is (A). The iodine number was estimated by using this equation:

$$\text{Iodine number} = \frac{(B - A) \times N \times (127) \times (40 \div 10)}{\text{wt of AC (g)}} \quad (2.3)$$

Where B= blank reading, A= burette reading, N= normality of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution (mole.L^{-1}), and wt. = mass of AC.

2.4.4.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy analysis was conducted for a number of adsorbent surfaces (CFAC, PFAC with Cu and Ni) using a field emission scanning electron microscopy (Jordan University of Science and Technology/Nanotechnology Institute) (JUST) with an energy dispersive x-

ray spectrometer (EDS). This was to study surface textures and EDX analysis of different solids A.C.

2.4.5 Experiments of adsorption:

Cu and Ni adsorption onto AC surfaces were studied by batch experiments. Experiments were conducted in a set of 100 mL flasks. After addition of Cu or Ni solution to AC, adjustment of the pH of the solutions, experiments flasks were shaken at 150 rpm using controlled temperature (Tuttnauer) water bath with a shaker. The flasks were left under constant-speed shaking for required time.

Initial pH of Cu and Ni solutions, used in experiments of adsorption, was adjusted by adding few drops of sodium hydroxide solution or sulphuric acid as required. pH measurement was done on a pH-meter.

2.4.5.1 Cu and Ni adsorption experiments

Stock solutions of: $\text{Cu}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ were prepared (1000 mg/L Cu or Ni) by dissolving a mass of 0.38 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 100 ml distilled water in a volumetric flask, and 0.311 g of $\text{Ni}(\text{NO}_3)_2$ in 100 ml distilled water in another volumetric flask. From these two solutions, different solutions (5-30 mg/L) were prepared by dilution. In each Ni or Cu adsorption experiments, an aliquot (20 mL) of these solutions was used. Ni and Cu concentrations were analyzed at the end of each experiment by AAS.

2.4.5.1.1 Effect of adsorbent dosage

Different amounts (0.10-0.60 g) of PFAC/NaHCO₃ and CFAC/H₃PO₄ (were placed into flasks, then solutions (20 mL, 25 mg/L Cu or Ni) were added to each flask and the pH was adjusted at 2. then were shaken for 1.5 hr. at 25°C.

2.4.5.1.2 Effect of initial pH:

Effect of pH on adsorption was studied in the pH range 2-12. The pH was varied, by adding NaOH or HCl solutions. Cu or Ni solutions (20 mL, 25 mg/L each) were added to *P.halepensis* and *Cupressus sempervirens* adsorbent samples (0.20 g) at 25°C for 1.5 hr.

2.4.5.1.3 Effect of temperature:

The effect of temperature on adsorption was studied. Cu and Ni solutions (20 mL, 25 mg/L each) were added to adsorbent samples (0.2 g) at pH 2. The mixtures were shaken for 1.5 hr. at different temperatures in the range 0-45°C.

2.4.5.1.4 Effect of time

Time effect on adsorption was studied. Cu, Ni solutions (20 mL, 25 mg/L) each was added to (0.2 g) of *Cupressus sempervirens* and *P.halepensis* adsorbent samples at pH 2. The solution was shaken at different time range (0.5- 48 hr.) at 25°C.

2.4.5.1.5 Effect of Cu, Ni concentrations

In each adsorption experiment, Ni and Cu contaminated water of a given concentration ranging from 5 to 30 ppm (Cu or Ni) were added to 0.20 g adsorbent, with initial pH 2. The flasks were shaken at 25°C for 1.5 h to reach equilibrium. The final concentrations of (Cu or Ni) were measured by AAS.

2.4.5.1.6 Langmuir and Freundlich Isotherms

The amount of adsorption at equilibrium, q_e (mg/g), was calculated by the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2.4)$$

Where: C_o (mg/L) is the liquid- phase conc. Of Cu, Ni at initial

C_e (mg/L): the liquid- phase conc., of Cu, Ni at equilibrium.

W: the mass of dry adsorbent used in (g), and equal 0.2g

V: the volume of solution in (L), and equal 0.2 L.

Two isotherms were used to evaluate the adsorption parameters: Langmuir and Freundlich.

Langmuir Equation:

Langmuir isotherm assumes a mono layer adsorption and homogenous adsorbent, that is mean the max., adsorption can be happened only by one molecule of adsorbate. In this isotherm adsorption is localized and has a uniform surface, so it has the same mechanism. [3, 37, 39]

Langmuir equation can be writing as the following:

$$\frac{C_e}{q_e} = \frac{1}{b Q_m} + \frac{C_e}{Q_m} \quad (2.5)$$

Where: q_e is the amount of Cu, Ni adsorbed by activated carbon at equilibrium (mg/g).

Q_m : the max amount of Cu, Ni, adsorbed per unit mass of A.C (mg/g).

C_e : Conc., at equilibrium of Cu, Ni (mg/L)

B : Langmuir constant (L/mg).

Freundlich isotherm assumes heterogeneous surface at equilibrium and not mono layer capacity. This isotherm is given by the following equation:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (2.6)$$

Where: q_e the amount of adsorbate per unit mass of adsorbent (mg/g).

K_f , n : Freundlich constants, which can be calculated from the plot of $\log q_e$ vs., $\log C_e$. (n) Is giving an indication of how favorable adsorption process is, and K_f : related the adsorption capacity of adsorbent ((mg/g) (L/mg) $1/n$)

The range of slope ($1/n$) between 0-1, it is measure heterogeneous surface, if the value gets closer to zero, that is mean becoming more heterogeneous.

2.4.6 Preparation of volatile oil

250 g of *Cupressus sempervirens* or *P.halepensis* was mixed with 150 ml of Deionized water (temp was 100°C, time 2 hr.), in around flask and transfer to microwave instrument to get volatile oil were it use in the antioxidant test.

2.4.7 Antioxidant activity

2.4.7.1 Trolox standard and plant working solution

DPPH test

10 mg of a volatile oil (*Cupressus sempervirens* and *P.halepensis*) was dissolved in 100 ml methanol to get a stock solution of 100 mg/L and then different standard solutions with concentrations (1, 2, 3, 5, 7, 10, 20, 30, 40, 50, and 80 µg/ml) were prepared by using methanol as a solvent. 2mg/100 ml methanol of 2, 2-diphenyl-1-picrylhydrazyl (DPPH) solution was freshly prepared. The final solution was 1:1:1 concentration ratio of working solution, methanol, and DPPH, then was placed in dark area for 30 minutes at 25 C [66].

2.4.7.2 Spectrophotometric measurement

The spectrophotometer was used and adjusted at 517 nm, the blank solution was methanol.

2.4.7.3 Percentage of inhibition of DPPH activity

DPPH inhibition percentage;

$$= \frac{(A - B)}{A} \times 100\% \quad (2.7)$$

Where A is the optical density of the blank

B is the optical density of the sample [67].

The antioxidant half maximal inhibitory concentration (IC_{50}) for the plant extracts as well as the standard deviation were both calculated using GraphPad Prism 6 Program

Chapter 3:

Results and Discussions

3.1 Iodine number surface areas

Table 5: Surface area of different AC according to iodine number test.

Types of Activation	Samples	Surface areas (mg/g) CFAC	Surface areas (mg/g) PFAC
Chemical Activation	ZnCl ₂	177.8	1003.3
	NaHCO ₃	594.4	1257.3
	NaOH	127	1130.3
	H ₃ PO ₄	762	986
Physical activation		508	444.5

The best surface area iodine numbers of the produced A.C types (*Cupressus sempervirens* and *P.halepensis*) were given in table 5. The largest surface areas of CFAC is 762 m²/g by using H₃PO₄ as activating agent, and PFAC are 1257.3 m²/g by using NaHCO₃ as activating agent.

3.2 Percentage yield of prepared CFAC and PFAC samples

Table 6: Percentage yield of prepared activated carbon

Sample No.	Sample Name	Activation Condition	%Yield
1	CFAC	Physical	69%
2	PFAC	Physical	35.5%
3	CFAC/ZnCl ₂	ZnCl ₂	50.4%
4	PFAC/ZnCl ₂	ZnCl ₂	45%
5	CFAC/NaHCO ₃	NaHCO ₃	65%
6	PFAC/NaHCO ₃	NaHCO ₃	68%
7	CFAC/NaOH	NaOH	40.6%
8	PFAC/NaOH	NaOH	33.3%
9	CFAC/ H ₃ PO ₄	H ₃ PO ₄	40%
10	PFAC/H ₃ PO ₄	H ₃ PO ₄	42%

3.3 Scanning Electron Microscopic (SEM) and EDX for AC

The surface physical morphology of CFAC and PFAC was examined by using (FE-ESM) Field Emission Scanning Electron Microscope. In the SEM analysis the samples were coated with Au (thin layer). The elemental composition of the sample was determined from SEM-EDX tests.

SEM

Scanning electron microscopy (SEM) process was employed to view the surface physical morphology of *Cupressus sempervirens* and *P.halepensis*

fruits derived A.C. fig.4: showed the (SEM) micrographs of the different modified AC of (CFAC/H₃PO₄, PFAC/NaHCO₃) with 1000-20000 magnification.

Pores of different shape and size could be observed from the micrograph. It can be seen the external and internal surface of the AC are full of pores in CFAC and PFAC. Also it can be seen that some Cu, Ni particles were scattered on the surface of AC, and trapped into the pores that caused high removal efficiency of 2 heavy metals (Cu, Ni).

These results indicated that the 2 plants can be used as alternative commercial AC due to high cavities and high surface area for purification of contaminated water.

All pictures can see clearly in Appendix (1).

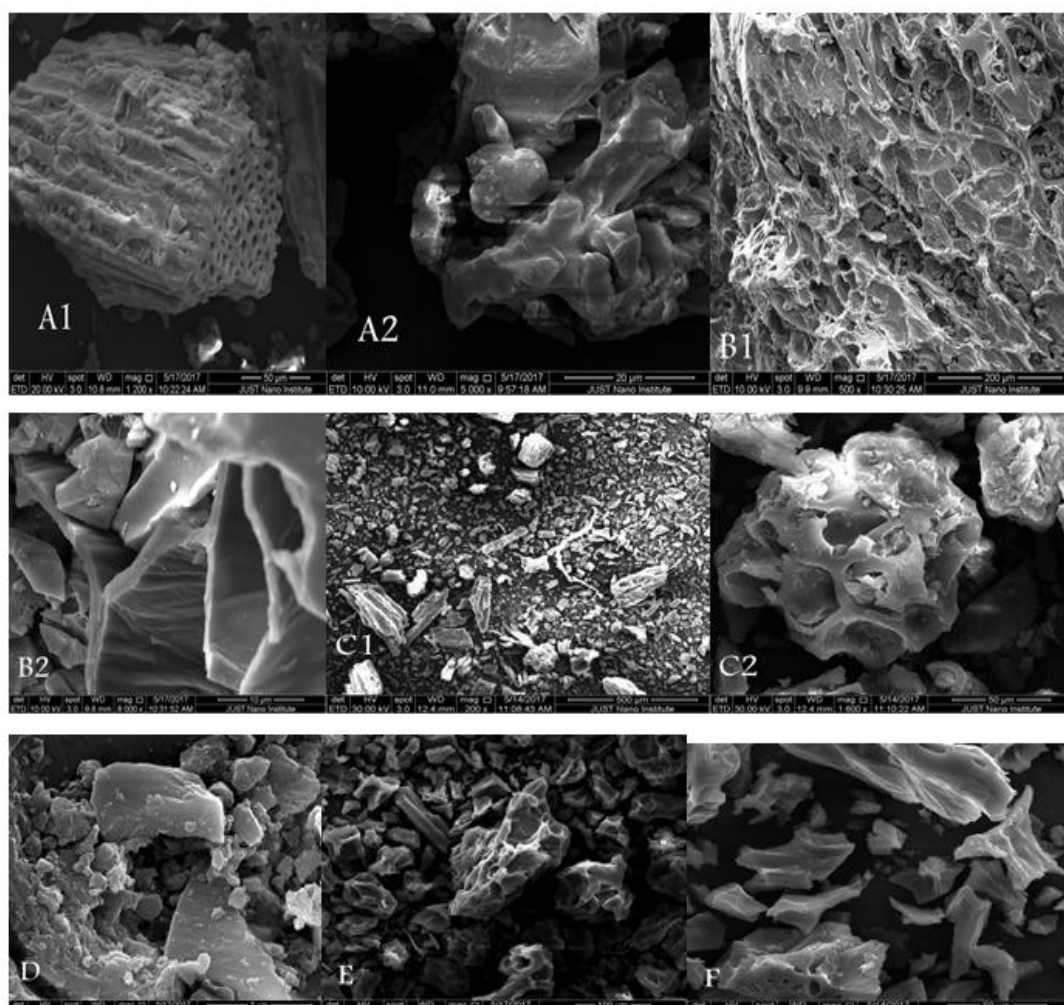


Fig.4: SEM micrographs of the most surface area in iodine test: A1, A2 (PFAC/NaHCO₃/Pure), B1, B2 (CFAC/H₃PO₄/Pure), C1, C2 (PFAC/NaHCO₃/Cu), D (PFAC/NaHCO₃/Ni), E (CFAC/H₃PO₄/Cu), F (CFAC/H₃PO₄/Ni)

EDX analysis:

Elemental analysis was done by energy dispersive X-ray [EDX] instrument with Scanning Electron Microscopy. It is a qualitative and semi-quantitative elemental composition.

An EDX spectroscopy was used to identify and quantify the present elements in sample. The X-axis was displayed energy [KeV], and the Y-axis was displayed counts or wave length.

X-rays is characteristic of the elements they come from, X-rays emitted from [carbon] for example will always have the same wave length and energy, so fall at the same position in spectrum. X-rays from elemental analysis present in sample appear to be counted simultaneously.

Fig.5: showed the good results for adsorption Ni in *P. halepensis*-NaHCO₃, the initial conc., of Ni was 25 ppm, and the max percentage removal of this metal= 98.5 at pH=7 and contact time 24 hr. The EDX analysis showed Ni in spite of it is very small conc., in comparison with carbon, that's indicated PFAC was high adsorption the heavy metal. Next figure showed the wave length, At% and wt% of the elements. Another figures in Appendix 2 showed the similar results for Cu, Ni before and after adsorption.

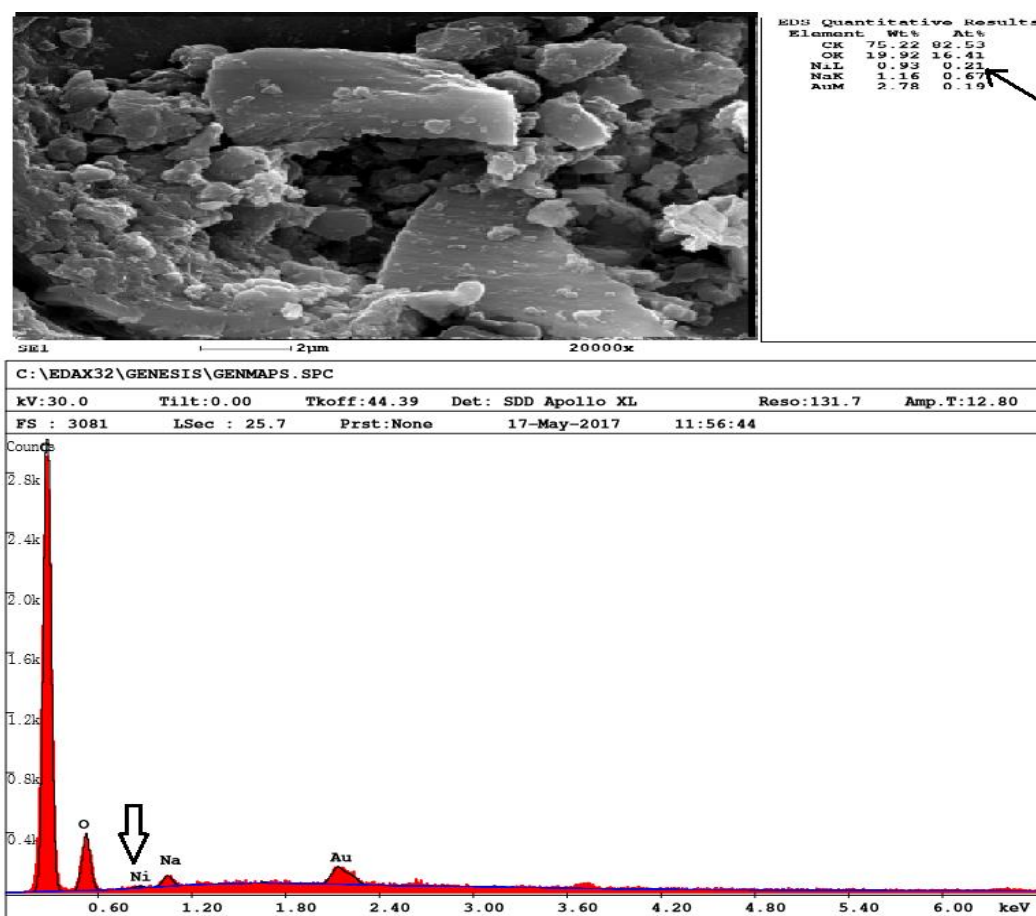


Fig.5: EDX analysis of CFAC- Ni adsorption

3.4 Adsorption of Cu on AC from *Cupressus sempervirens*, *P.halepensis*, and Commercial AC

3.4.1 Effect of contact time:

The effect of different contact time on Cu removal was shown in Fig.6

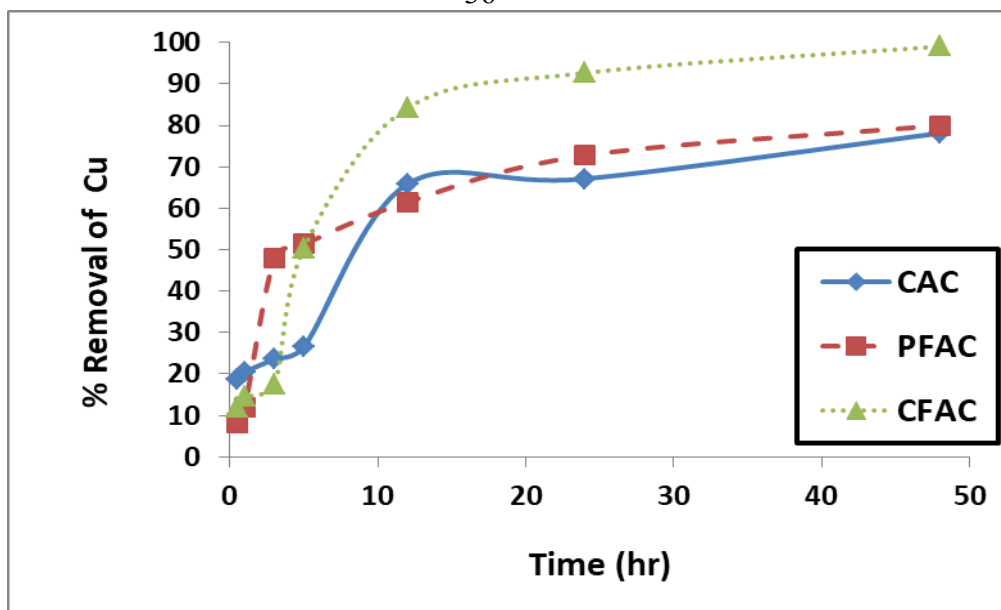


Fig.6: Effect of contact time on Cu solution removal by CFAC, PFAC and CAC at (initial conc. 25 mg/L, pH: 2, temperature: 25 °C and 0.2 g of each AC).

The adsorbed amount of Cu onto PFAC, CFAC and CAC increases with the increase of time, as shown in Fig. 6, and the Cu adsorption reached equilibrium in about 35 hr. for CFAC, 48 hr. for PFAC and 48 hr. for CAC. Adsorption capacity for Cu showed a rapid increase in adsorbed amount during the first 5 hr. This adsorption capacity at the few hours by CFAC and PFAC indicated higher driving force that making rapid transfer of Cu to the surface of CFAC and PFAC in comparison with CAC. From this figure the % removal of Cu using CFAC was 99%, PFAC it was 80% and CAC 78%. So this indicated to use CFAC and PFAC than CAC.

3.4.2 Effect of adsorbent dosage:

The impact of CFAC, PFAC and CAC dosage on Cu removal using 0.1 to 0.6g adsorbent dosage at an adsorption time of 1.5 hr. is shown in Fig.7. The percent of Cu removal of CFCA was 95% of (0.6g /20ml). For three types of adsorbents increase the dosage increase the percent of removal.

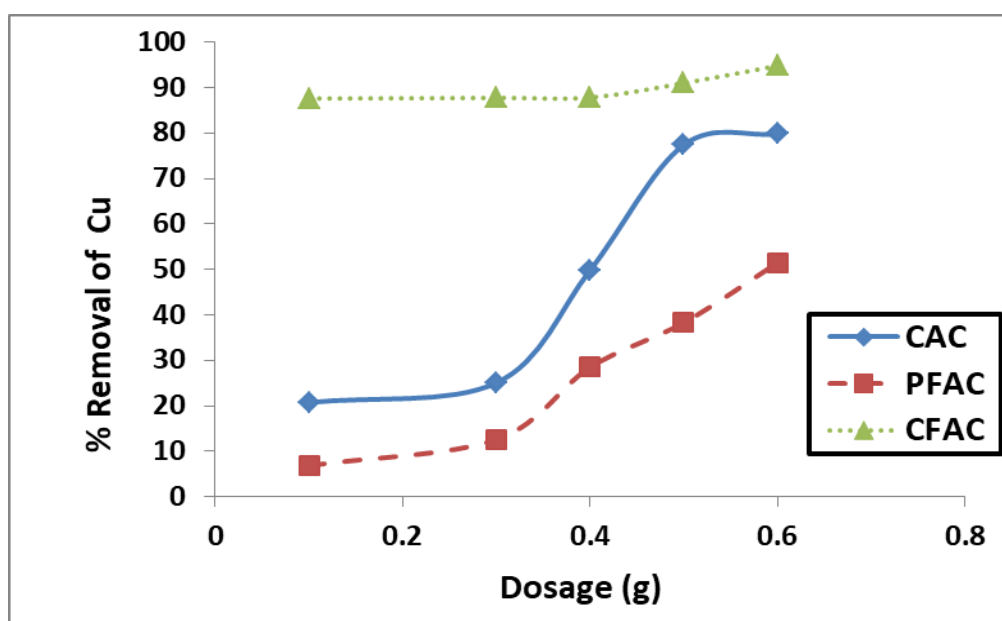


Fig7: Effect of adsorbent dosage on Cu removal by CFAC, PFAC and CAC at (conc. 25 mg/L, pH: 2, temperature: 25 °C and contact time: 1.5 hr.).

3.4.3 Effect of pH:

The variation of adsorption using CFAC and PFAC was investigated in the pH range 2-12 using sulfuric acid and sodium hydroxide to control pH. The effect of pH on Cu removal was studied, using 0.2g CFAC, PFAC and CAC at an adsorption time of 1.5 hr. to reach equilibrium, fig.8 summarized these results:

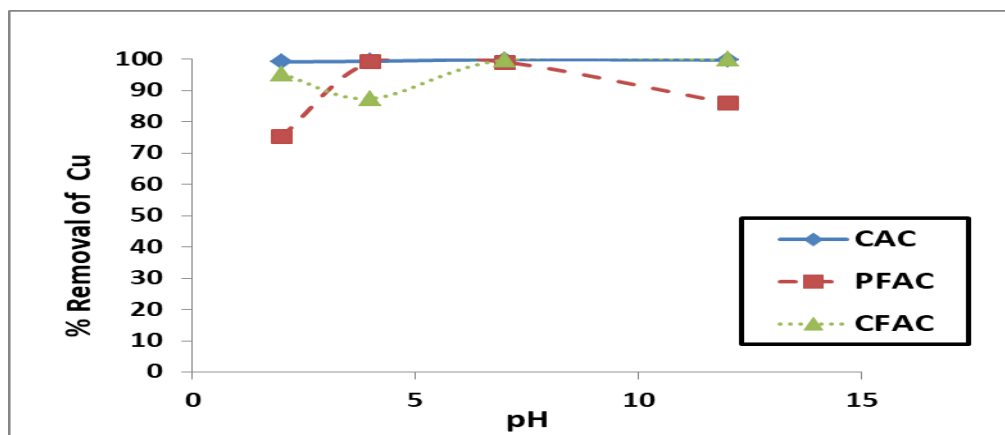


Fig.8: Effect of pH on Cu removal by CFAC, PFAC and CAC at (initial conc. 25 mg/L, temperature: 25 °C, contact time: 1.5 hr.)

For each adsorbent, the perfect pH for the removal of Cu was 7,12,7 for PFAC, CFAC, CAC, respectively.

3.4.4 Effect of Temp

The effect of temperature on adsorption onto CFAC, PFAC and CAC was studied in the range of 0-45 °C. The results are shown in Fig.9.

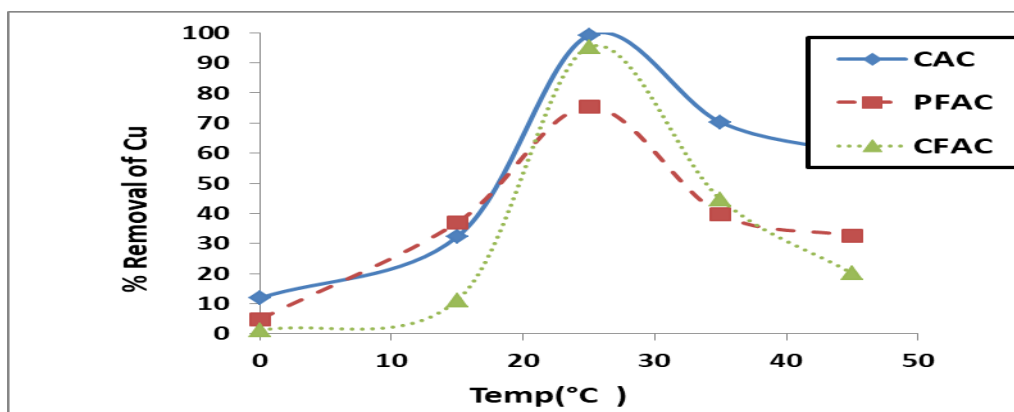


Fig.9: Effect of temperature on Cu removal by CFAC, PFAC and CAC at (initial conc.25 mg/L, pH: 2, contact time: 1.5 hr. and 0.2g dosage)

The results showed that the suitable temperature is 25°C, the percent of removal Cu at 25°C was 95, 75, and 99 for CFAC, PFAC and CAC, respectively so this indicated to use CFAC because it's the percentage is near CAC.

Increase temp decrease the percent of removal of Cu due to lessening of its physical interaction with the adsorbent, and the attraction between each of AC with the adsorbent reduced.

3.4.5 Effect of concentration

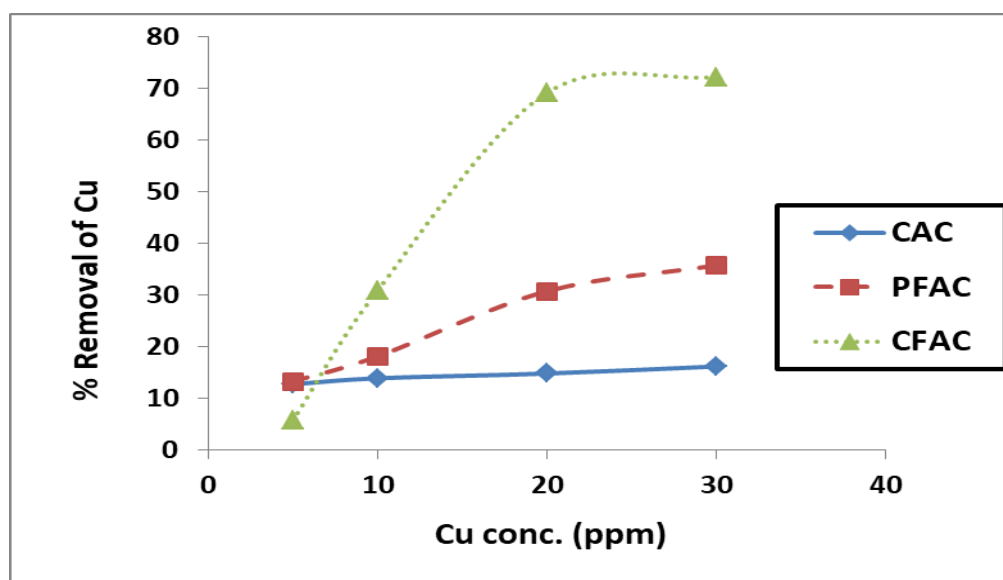


Fig.10: Effect of Cu concentration on % removal by CFAC, PFAC, and Charcoal at (initial adsorbent dose: 0.2 g, initial pH: 2, contact time: 1.5 hr., Temperature 25 °C).

Fig.10 showed the effect of initial concentration of Cu on the percentage removal at equilibrium. This figure showed that the increase of concentration of Cu increased the percentage of Cu removal, by PFAC, CFAC and Charcoal.

As Cu concentration increases from 5 mg/L to 30 mg/L, the percentage removal was increased from 13 % to 36% for PFAC and from 6% to 72% for CFAC.

3.5 Adsorption of Ni on AC from *Cupressus sempervirens*, *P.halepensis*, and Commercial

3.5.1 Effect of contact time

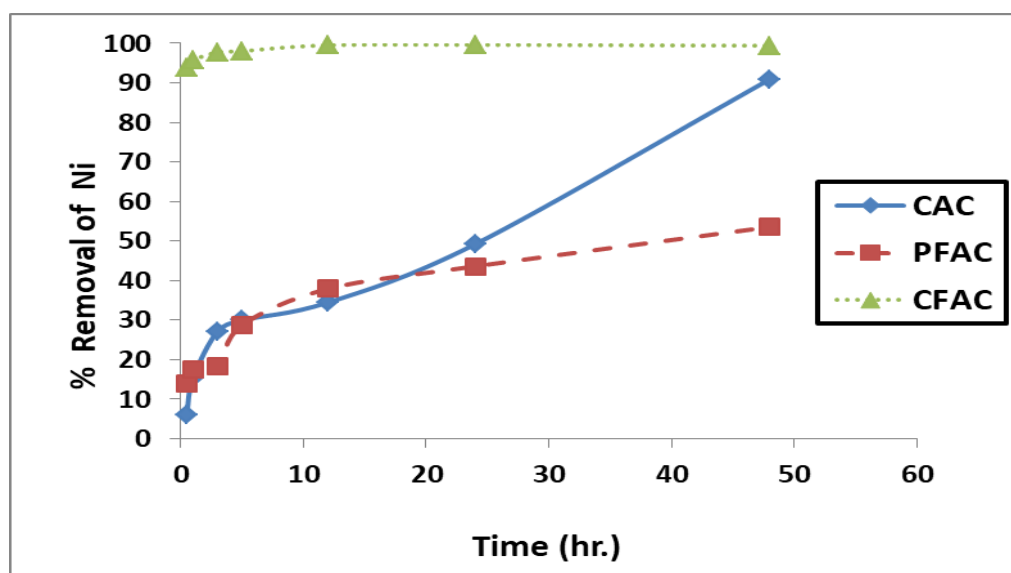


Fig.11: Effect of contact time on Ni solution removal by CFAC, PFAC and CAC at (initial conc. 25 mg/L, pH: 2, temperature: 25 °C and 0.2 g of each AC).

The adsorbed amount of Ni onto PFAC, CFAC and CAC increased with the increase of time, as shown in Fig.11, and the Ni adsorption reached equilibrium in about 40 hr. for PFAC, 12 hr. for CFAC and 48hr for CAC. Adsorption capacity for Ni showed a rapid increase in adsorbed amount during the first 0.5 hr. for CFAC and 3 hr. for CAC and PFAC. This

adsorption capacity at the few hours by CFAC and PFAC indicated higher driving force that making rapid transfer of Cu to the surface of CFAC and PFAC comparing with CAC. From this figure the % removal of Ni using CFAC was 99.6%, PFAC it was 53.5% and CAC 90%. So this indicated to use CFAC than CAC.

3.5.2 Effect of adsorbent dosage

The effect of CFAC- H_3PO_4 , PFAC- NaHCO_3 and CAC on Ni removal was studied, using 0.1- 0.6 g AC at an adsorption time of 90 min. the results are summarized in Fig.12

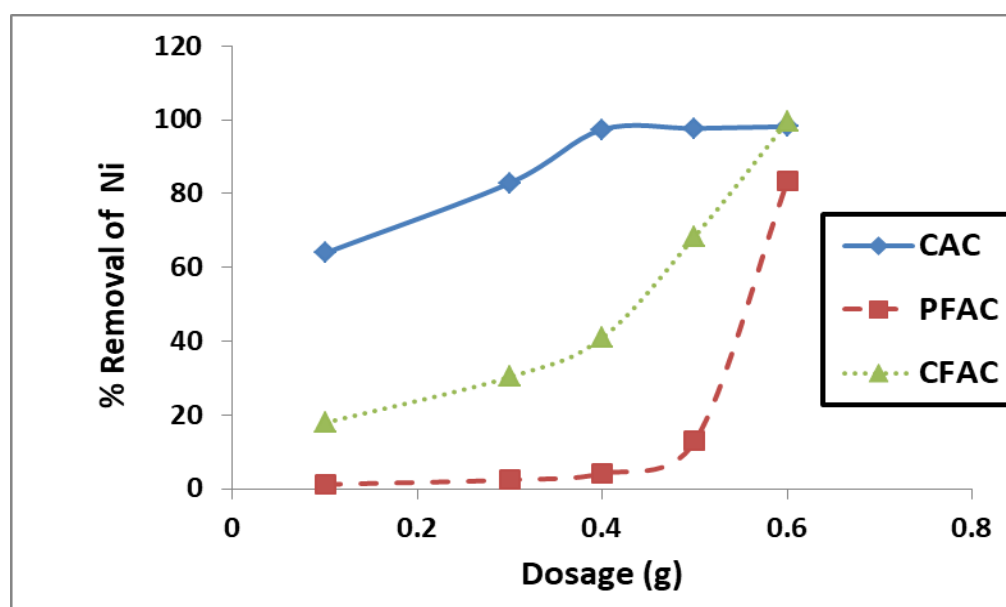


Fig.12: Effect of adsorbent dosage on Ni removal by CFAC, PFAC and CAC at (conc.

25 mg/L, pH: 2, temperature: 25 °C and contact time: 1.5 hr.).

The percent of Ni removal increased by increasing adsorbent dosage. Adsorption increased up to 99% of CFAC, 83% of PFAC and 98% of CAC with adsorbent dosage (0.6 g /20 mL) because increasing adsorbent dosage

at stable Ni conc. produced more adsorption sites and thus increased of Ni removal. In this result the CFAC is better adsorbent than CAC at the same dosage.

3.5.3 Effect of pH

Fig.13 summarized the results of Ni adsorption in the pH range 2-12, at constant time 1.5 hr., and 0.2 dosages in (25 ppm / 20mL) of Ni solution.

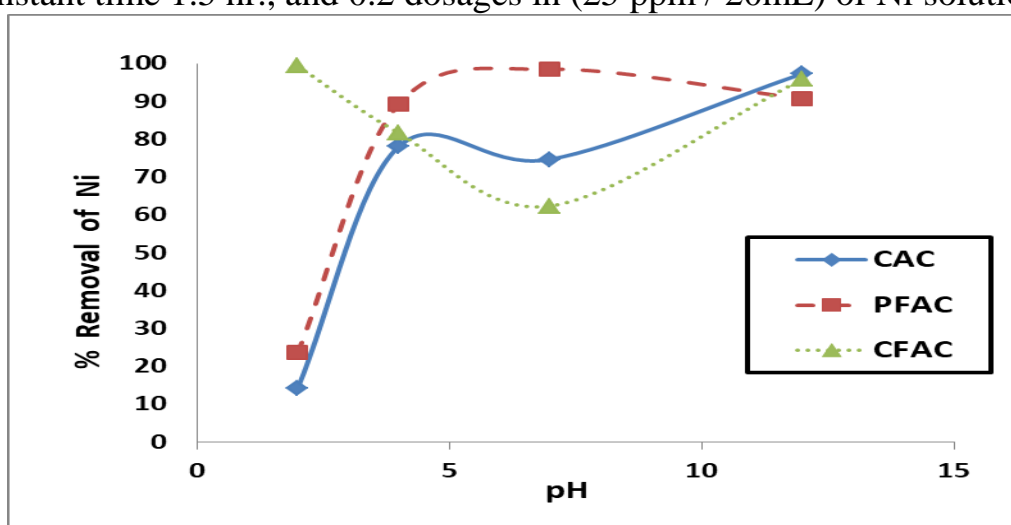


Fig.13: Effect of pH on Ni removal by CFAC, PFAC and CAC at (initial conc. 25 mg/L, temperature: 25 °C, contact time: 1.5 hr)

In this results percentage removal of Ni are 99.4%, 98.6% and 97.4% for CFAC, PFAC and CAC respectively.

3.5.4 Effect of temp

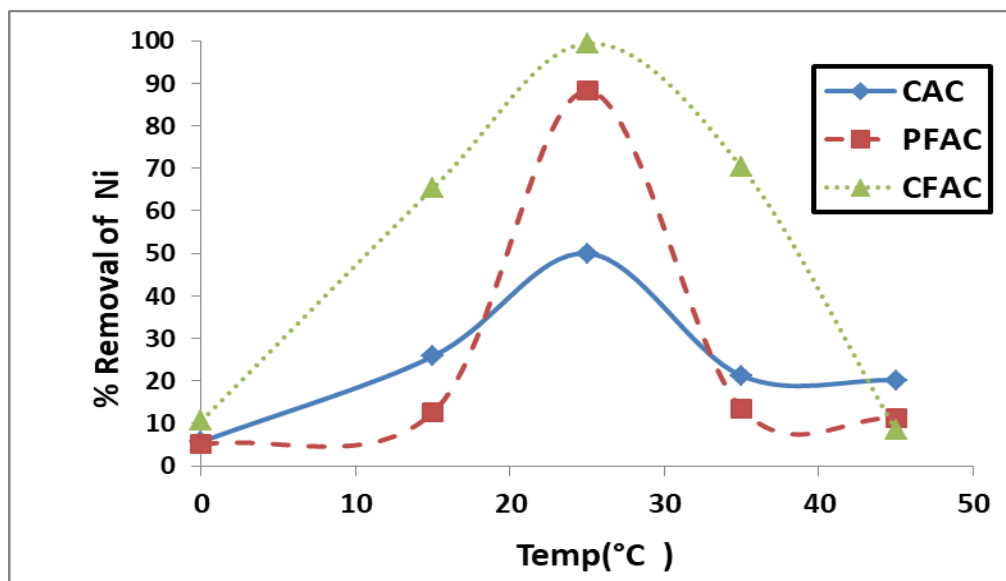


Fig.14: Effect of temperature on Ni removal by CFAC, PFAC and CAC at (initial conc.25 mg/L, pH: 2, contact time: 1.5 hr. and 0.2g dosage)

The different range temperature was studied to calculate % removal of Ni by using 0.2 g at 1.5 hr. The best temperature in figure 15 was 99.4%, 88.2%, and 50% of CFAC, OFAC, and CAC respectively at 25 °C. CFAC and PFAC were excellent removal of Ni compared with CAC.

3.5.5 Effect of concentration

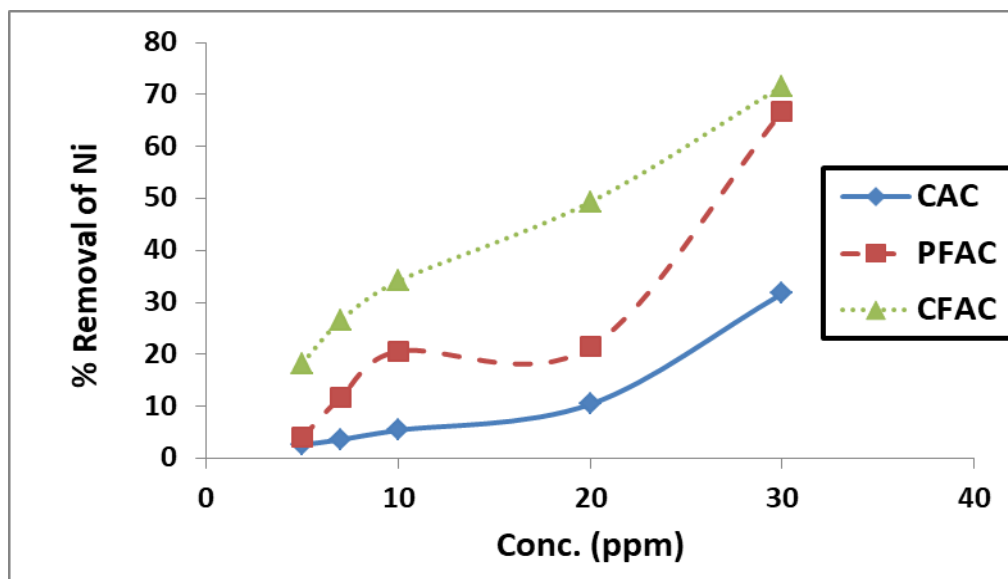


Fig.15: Effect of Ni concentration on % removal by CFAC, PFAC, and Charcoal at (initial adsorbent dose: 0.2 g, initial pH: 2, contact time: 1.5 hr., Temperature 25 °C).

Fig.15 showed the effect of concentration range from 5-30 ppm, the increase of concentration increases the percentage of Ni removal. As Ni concentration increased from 5 mg/L to 30 mg/L, the % removal was increased from 18.3% to 71.6% for CFAC and from 4% to 66.7% for PFAC.

3.5.6 Best parameters and max removal of Cu for different AC types

Table 7: Best parameters and max removal of Cu for different A.C types

AC types	Parameters and max Removal									
	pH	Max removal %	Conc. mg/L	Max removal %	Time min.	Max removal %	Temp °C	Max removal %	Dosage g	Max removal %
CFAC	12	99.98	30	72.2	48	99.06	25	95.32	0.6	94.78
PFAC	4	99.15	30	35.7	48	80	25	75.4	0.6	51.48
CAC	7	99.9	30	16.13	48	78.1	25	99.2	0.6	79.8

3.5.7 Best parameters and max removal of Ni for different A.C types

Table 8: Best parameters and max removal of Ni for different A.C

AC types	Parameters and max Removal									
	pH	Max removal %	Conc. mg/L	Max removal %	Time min.	Max removal %	Temp °C	Max removal %	Dosage g	Max removal %
CFAC	2	99.4	30	71.6	48	99.6	25	99.4	0.6	99.5
PFAC	7	98.58	30	66.73	48	53.54	25	88.2	0.6	83.33
CAC	12	97.4	30	31.7	48	90.9	25	50	0.6	98.2

3.6 Adsorption isotherm on CFAC, and PFAC

Adsorption isotherms give an idea about adsorption capacity, so it is important to study. In this research, Langmuir and Freundlich isotherm models were used to describe the relationship between the amounts of Cu, Ni adsorbed and its equilibrium concentration in solution at 25°C. To determine adsorption data Langmuir and Freundlich isotherm equations was investigated by plotting C_e/q_e vs. C_e for Langmuir, and $\log q_e$ vs. $\log C_e$ for Freundlich.

3.6.1 Langmuir and Freundlich Isotherms for Cu

The Langmuir and Freundlich isotherms parameters which were calculated from the slope and intercept of the linear plots using the linearized of the Langmuir (equation 2.5) and Freundlich (equation 2.6), with the R^2 values were given in figures 16,17, for Cu and table 9 had compared the different parameters with different activated carbons.

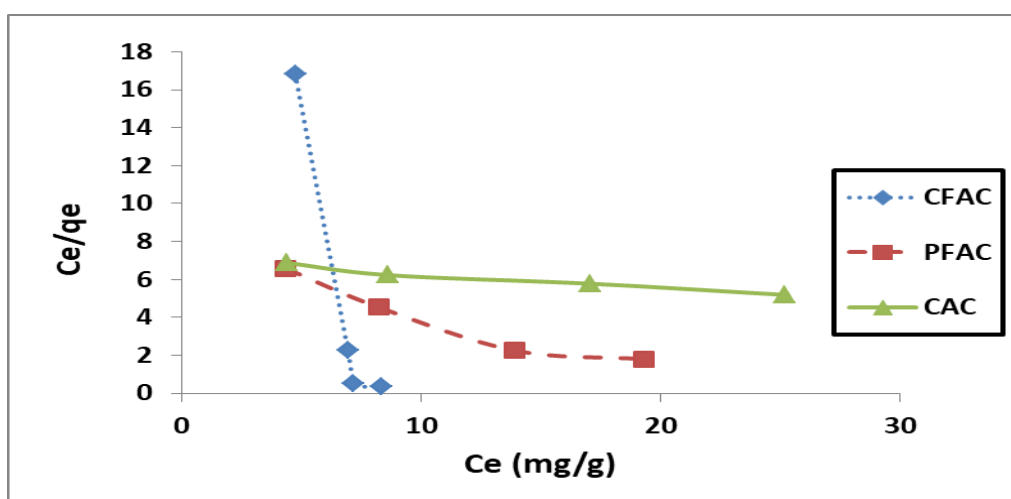


Fig.16: Langmuir plot for Cu adsorption onto CFAC, PFAC and CAC at (temp:

25 °C, initial pH: 2 and solid/ liquid ratio 0.2 g/20 mL)

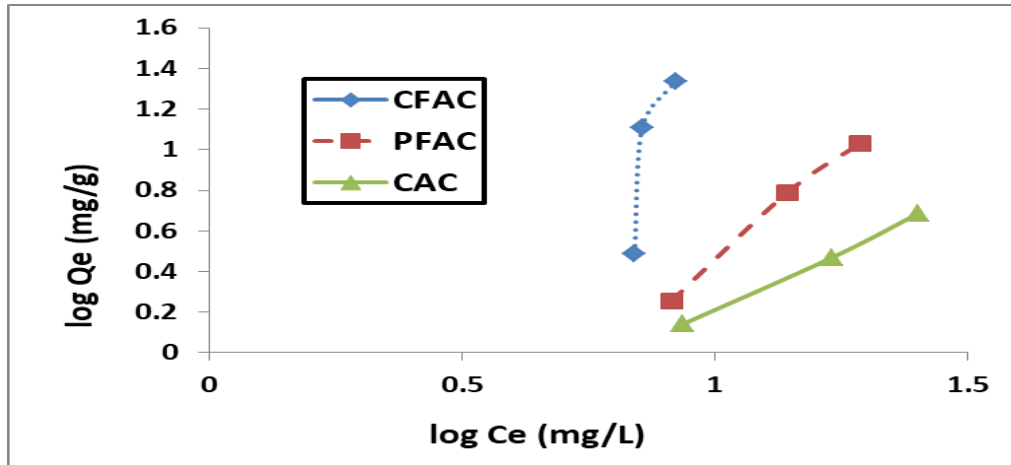


Fig.17: Freundlich plot for Cu adsorption onto CFAC, PFAC and CAC at (temp: 25 °C, initial pH: 2 and solid/liquid ratio 0.2 g/20mL).

Table 9: Langmuir and Freundlich is isotherm model parameters and correlation coefficient of Cu adsorption onto: CFAC, PFAC and CAC

Isotherm		Langmuir				Freundlich			
	A.C	Parameters				Parameters			
		Equation	Q (mg/g)	b (L/mg)	R ²	Equation	K _f ((mg/g)(L/mg)) ^{1/n}	n	R ²
Cu Adsorbate	CFAC	y = -4.9281x + 38.449	-0.2	-0.13	0.878	y = 8.3783x - 6.3306	4.67*10 ⁻⁷	0.119	0.676
	PFAC	y = -0.3231x + 7.4834	-3.09	-0.04	0.919	y = 2.1027x - 1.6502	0.022	0.475	0.993
	CAC	y = -0.076x + 7.0684	-13.15	-0.01	0.963	y = 1.1624x - 0.9505	0.112	0.86	0.998

Langmuir isotherm gave negative values, that was indicated the inadequacy of the model of isotherm.

Data in table 9 indicated the fitting of the Freundlich to this adsorption process. In general, adsorption capacity depends on: K_f, if K_f increase the

adsorption capacity increased, (n) values in three A.C types is closer to zero, so that means becoming more heterogeneous.

The heterogeneous of CFAC, PFAC, CAC can be ranked in the following order $CFAC > PFAC > CAC$.

The R^2 value showed that adsorption with increase with increasing Cu conc., and the adsorption occurs in multilayer. The max value of R^2 from the table was for *P.halepensis*, $R^2 = 0.993$

3.6.2 Langmuir and Freundlich Isotherms for Ni

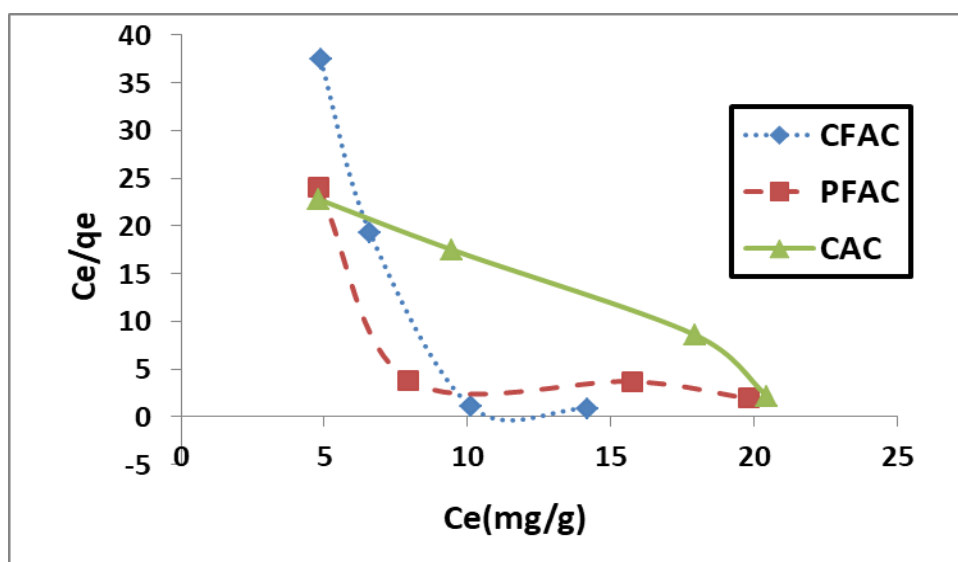


Fig.18: Langmuir plot for Ni adsorption onto CFAC, PFAC and CAC at (temp: 25 °C, initial pH: 2 and solid/liquid ratio 0.2 g/20mL).

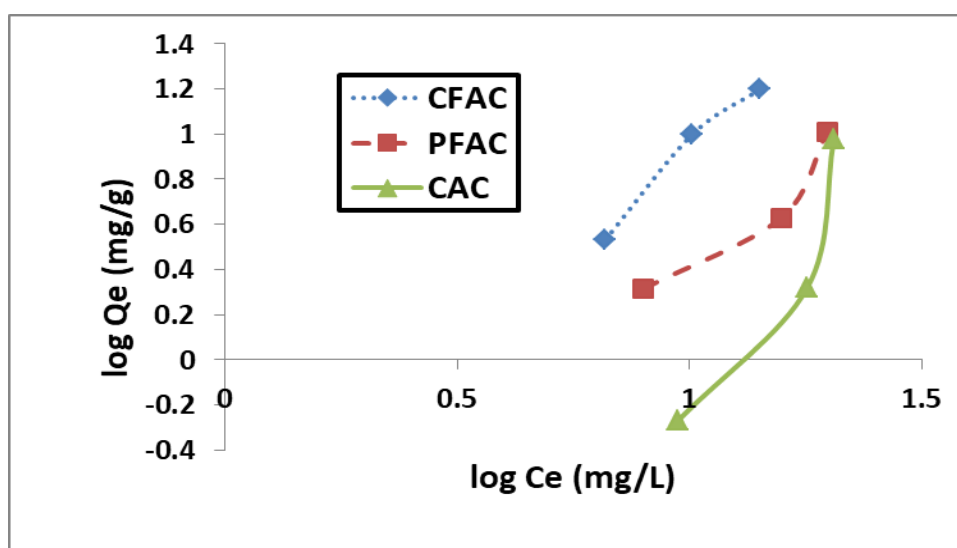


Fig.19: Freundlich plot for Ni adsorption onto CFAC, PFAC and CAC at (temp: 25 °C, initial pH: 2 and solid/liquid ratio 0.2 g/20mL).

Table10: Langmuir and Freundlich is isotherm model parameters and correlation coefficient of Ni adsorption onto: CFAC, PFAC and CAC

Isotherm		Langmuir				Freundlich			
		Parameters				Parameters			
	A.C	Equations	Q (mg/g)	b (L/mg)	R ²	Equations	K _f ((mg/g)(L/mg)) ^{1/n}	N	R ²
Ni Adsorbate	CFAC	y = -3.7608x + 48.334	-0.26	-0.07	0.789	y = 0.08 + 2.0197x - 1.0944		0.495	0.976
	PFAC	y = -1.13x + 22.016	-0.88	-0.05	0.557	y = 0.07 + 1.591x - 1.1495		0.628	0.892
	CAC	y = -1.246x + 29.161	-0.8	-0.04	0.977	y = 3.57* + 3.212x - 3.4469 - 10 ⁻⁴		0.311	0.850

Figures 18, 19 and table10 show the Langmuir and Freundlich isotherms for three types of A.C: CFAC, PFAC and CAC, of Ni adsorption.

The value from the table indicate Freundlich isotherm is better than Langmuir, due to the parameters of Langmuir have negative value. The most adsorption capacity was for CFAC because has max K_f value= 0.08.

(R^2) value for three types of A.C can be ranked in the following order:

CFAC>PFAC >CAC.

It was indicator the adsorption of CFAC occurs in more multilayer than others.

The results of *Cupressus sempervirens* comparing with the results of Nadeem Bassalat thesis, his thesis had the title "Treatment of Organic Phenolic Contaminant In wastewater Using Activated Carbon from *Cupressus sempervirens* Products". The next table summarized it.

Table 11: this work results vs. Nadeem Basalat results thesis

Work name	adsorbate	A.C modified	Activating agent	Optimum % removal	Best isotherms
This work	Cu Ni	<i>Cupressus sempervirens</i> and <i>P.halepensis</i>	H ₃ PO ₄ and NaHCO ₃	99.7% for Cu 99.4% for Ni	Freundlich
Nadeem results thesis	PNP (p-nitro phenol)	<i>Cupressus sempervirens</i>	H ₃ PO ₄	90.9% for PNP	Langmuir

3.7 Antioxidant activity

Free radical activity of the volatile oil of *Cupressus sempervirens* and *P.halepensis* in Palestine was studied using DPPH method, and Trolox was used as standard from this test IC_{50} was calculated.

3.7.1 Antioxidant activity and IC_{50} for *Cupressus sempervirens* and Trolox

Different concentrations were studied to calculate % inhibition DPPH, the concentration range from (0-100 μ g/mL). Fig.20 showed DPPH inhibition activity of Trolox standard and *Cupressus sempervirens* volatile oil from three different regions in Palestine.

Table 12: Percentage inhibition activity for Trolox and *Cupressus sempervirens* in Palestine

Conc. μ g/ml	% Inhibition by Trolox	% Inhibition by <i>Cupressus</i> <i>sempervirens</i> - north Palestine	% Inhibition by <i>Cupressus</i> <i>sempervirens</i> - middle Palestine	% Inhibition by <i>Cupressus</i> <i>sempervirens</i> - south Palestine
1	0	53.10	51.72	54.25
2	40.6	53.2	52.87	55.40
3	48.7	53.79	51.49	54.25
5	56.09	54.71	53.10	54.94
7	60.12	54.25	53.10	55.17
10	80.12	56.20	52.64	55.63
20	87.56	58.16	54.36	58.39
30	88.21	58.16	56.78	59.31
40	91.05	58.16	59.08	59.08
50	91.46	58.16	60.45	59.08
80	99.05	58.16	60.91	59.31
100	99.05	58.16	60.91	59.31

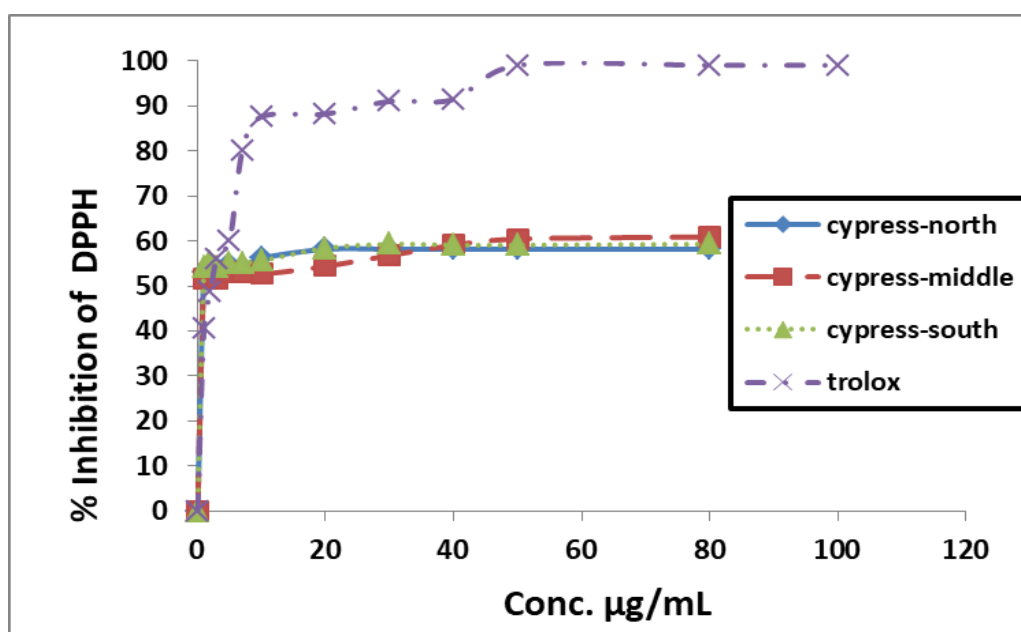


Fig.20: Antioxidant inhibition activity of Trolox standard and *Cupressus sempervirens* in Palestine.

Next table 13 shows the IC_{50} value for different regions *Cupressus sempervirens* volatile oil.

Table13: IC_{50} value and equation of *Cupressus sempervirens* volatile oil in Palestine

Areas	Equations	IC_{50} (µg/mL)
North	$Y = 13.257x + 39.18$	6.50
Middle	$Y = 14.86x + 36.548$	8.0398
South	$Y = 13.708x + 39.156$	6.181
Trolox	$Y = 38.651x + 32.84$	2.779

The most volatile oil sample was from the south because the IC_{50} was closest value to IC_{50} Trolox, and it means that south- *Cupressus sempervirens* in Palestine has high antioxidant activity than other regions.

The Antioxidant of *Cupressus sempervirens* volatile oil can be ranked in the following order:

Samples Trolox > *Cupressus sempervirens* - south Palestine > *Cupressus sempervirens* - north Palestine > *Cupressus sempervirens* - middle Palestine

3.7.2 Antioxidant activity and IC₅₀ for *P.halepensis* and Trolox

The free radical activity of the volatile oil of *P.halepensis* in three different regions in Palestine (north, middle and south) was tested using DPPH radical assay and Trolox as a reference.

Table14: Percentage inhibition activity for Trolox and *P.halepensis* in Palestine

Conc. μg/ml	% Inhibition by Trolox	% Inhibition by <i>P.halepensis</i> - north Palestine	% Inhibition by <i>P.halepensis</i> - middle Palestine	% Inhibition by <i>P.halepensis</i> - south Palestine
1	0.00	63.90	58.04	49.65
2	40.60	66.55	57.01	51.26
3	48.70	64.13	56.78	51.03
5	56.09	63.90	55.97	50.57
7	60.12	55.28	59.31	52.64
10	80.12	65.86	56.32	51.26
20	87.56	70.00	58.39	52.18
30	88.21	67.47	56.89	54.02
40	91.05	66.09	54.13	55.51
50	91.46	69.42	54.13	55.26
80	99.05	64.36	54.25	55.28
100	99.05	64.36	54.25	55.28

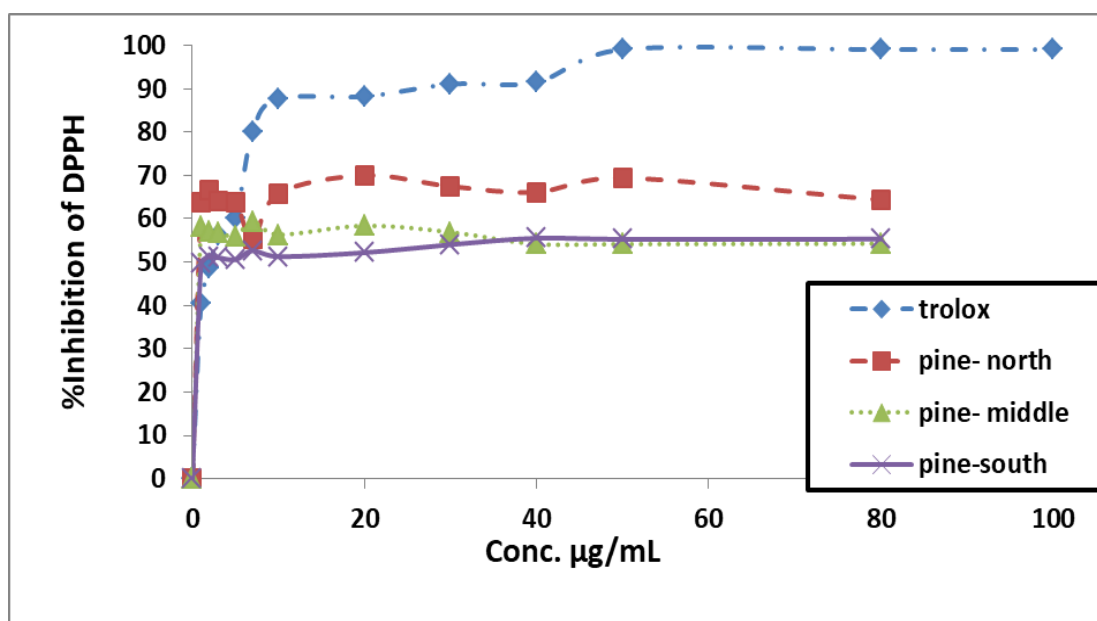


Fig.21: Antioxidant inhibition activity of Trolox standard and *P.halepensis* in Palestine.

The result of % Inhibition showed in fig. 21 and next table 15 gave IC_{50} value, the most potent volatile oil sample was from the north because IC_{50} was the closest value to IC_{50} Trolox.

Table15: IC_{50} value and equation of *P.halepensis* volatile oil in Palestine

Areas	Equations	IC_{50} (µg/ml)
North	$Y = 14.417x + 46.17$	1.844
Middle	$Y = 9.6531x + 42.678$	5.735
South	$Y = 12.747x + 36.217$	12.057
Trolox	$Y = 38.651x + 32.84$	2.779

The antioxidant of *P.halepensis* volatile oil sampled can be ranked of the following order:

P.halepensis - north Palestine > Trolox reference > *P.halepensis* - middle Palestine > *P.halepensis* - south Palestine

3.7.3 Percentage yield of *Cupressus sempervirens* volatile oil by ultrasonic microwave cooperative extractor/ reactor

Table 16: Percentage yield of *Cupressus sempervirens* volatile oil by ultrasonic microwave cooperative extractor/ reactor

Power	Time (hr.)	Temp (°C)	Wt. (mg)	percentage yield
1000	2	100	172 mg	0.0688
700	2	100	280 mg	0.112
500	2	100	Zero	Zero

Table 16: showed the percentage yield of *Cupressus sempervirens* volatile oil, 250 g of *Cupressus sempervirens* fruit and 150 mL of deionized water was added to microwave to extract volatile oil at different power (500, 700, 1000), and fixed time and temp (2 hr./100 °C) the power 700 was the best yield of the volatile oil.

Chapter 4

Conclusion and Recommendations

Conclusion:

- ✓ Activated carbon produced from *Cupressus sempervirens* and *P. halepensis* fruits gave a highest adsorption capacity when activated by H_3PO_4 , NaHCO_3 for *Cupressus sempervirens* and *P. halepensis*, respectively.
- ✓ Optimum percent of Cu removal 99.9% when CFAC (dosage 0.2g, at pH=12) and Ni removal 99.6 % (dosage 0.2g,).
- ✓ Optimum percent of removal 99.1% when PFAC (dosage 0.2g, at pH=4) and Ni removal 98.5% at pH=7.
- ✓ The results showed that equilibrium time for Cu, Ni adsorption on CFAC and PFAC is 24 hr.
- ✓ The optimum Temp for *Cupressus sempervirens* and *P. halepensis* is 25°C.
- ✓ Freundlich model describes the suitable adsorption isotherm of Cu, Ni onto CFAC, PFAC more efficiently than Langmuir model.
- ✓ The max IC50 value is for *Cupressus sempervirens* - south Palestine, and *P.halepensis* - north Palestine because closest for Trolox reference.
- ✓ The max yield of *Cupressus sempervirens* volatile oil by ultrasonic microwave cooperative extractor (at power 700, temp 100 °C and time 2 hr.).

Recommendation:

This work gave good and new results, for *Cupressus sempervirens* and *P.halepensis* Activated Carbon and antioxidant test. Recommendations for future researches include: Studying the adsorption this prepared activated carbon for different heavy metals and other activating agents, studying other parts of *Cupressus sempervirens* and *P. halepensis* as activated carbon such as sawdust and roots, studying chemical composition and pharmaceuticals benefits.

On the other hand, studying phytochemical screening extracts in different area in Palestine because get different results in DPPH- antioxidant, and studying the composition of volatile oil in different area use GC-MS, also antibacterial effects. Studying medical applications of plants (*Cupressus sempervirens* and *P. halepensis*).

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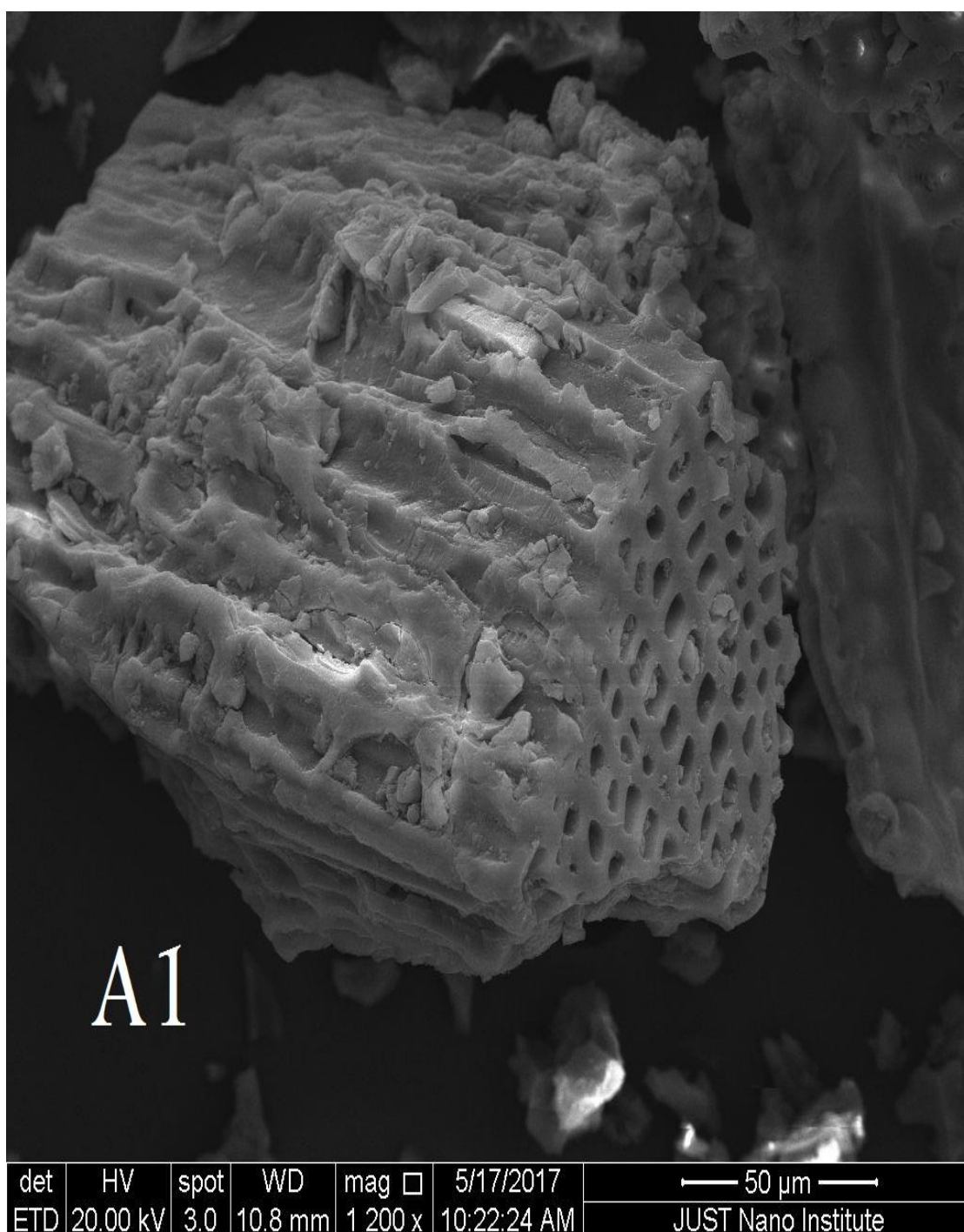
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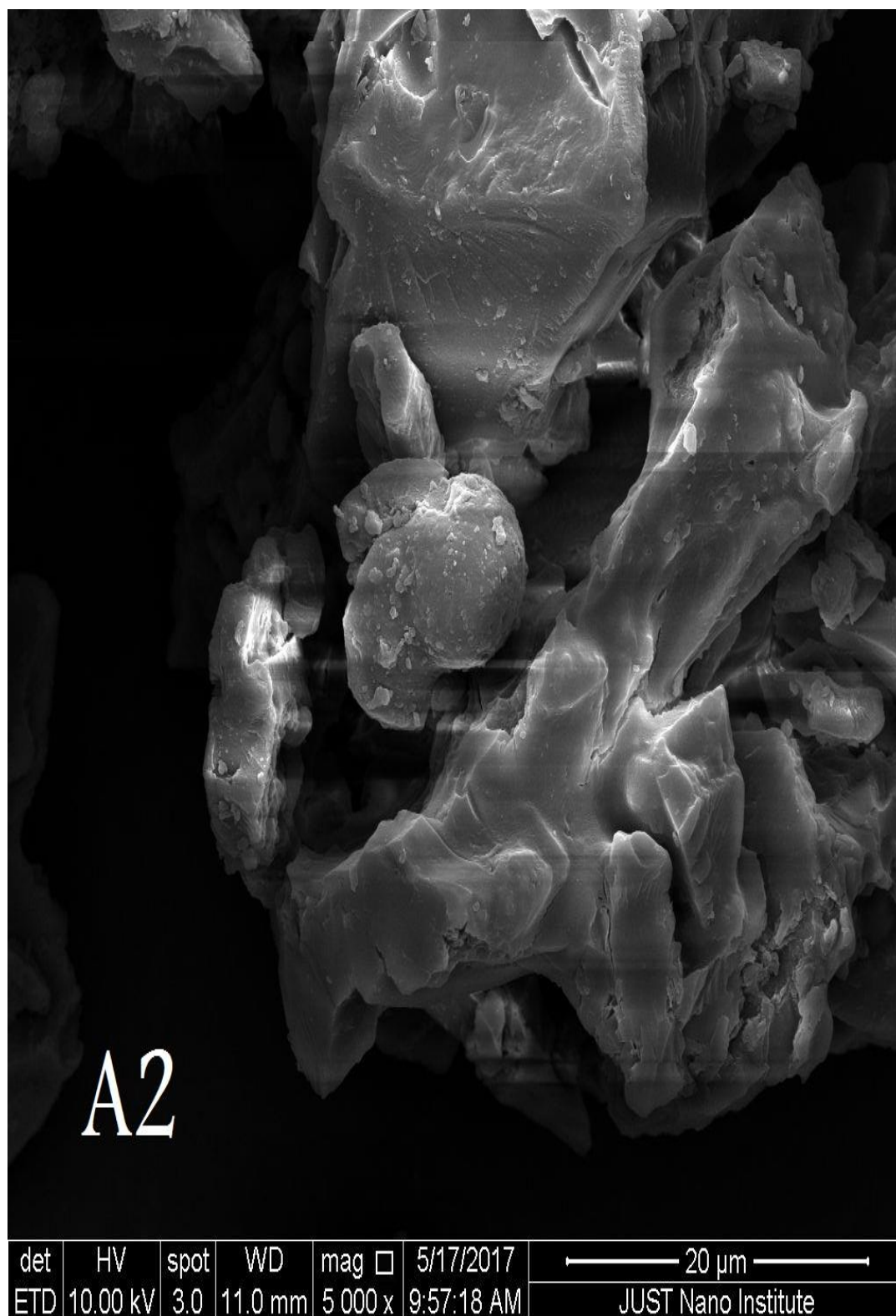
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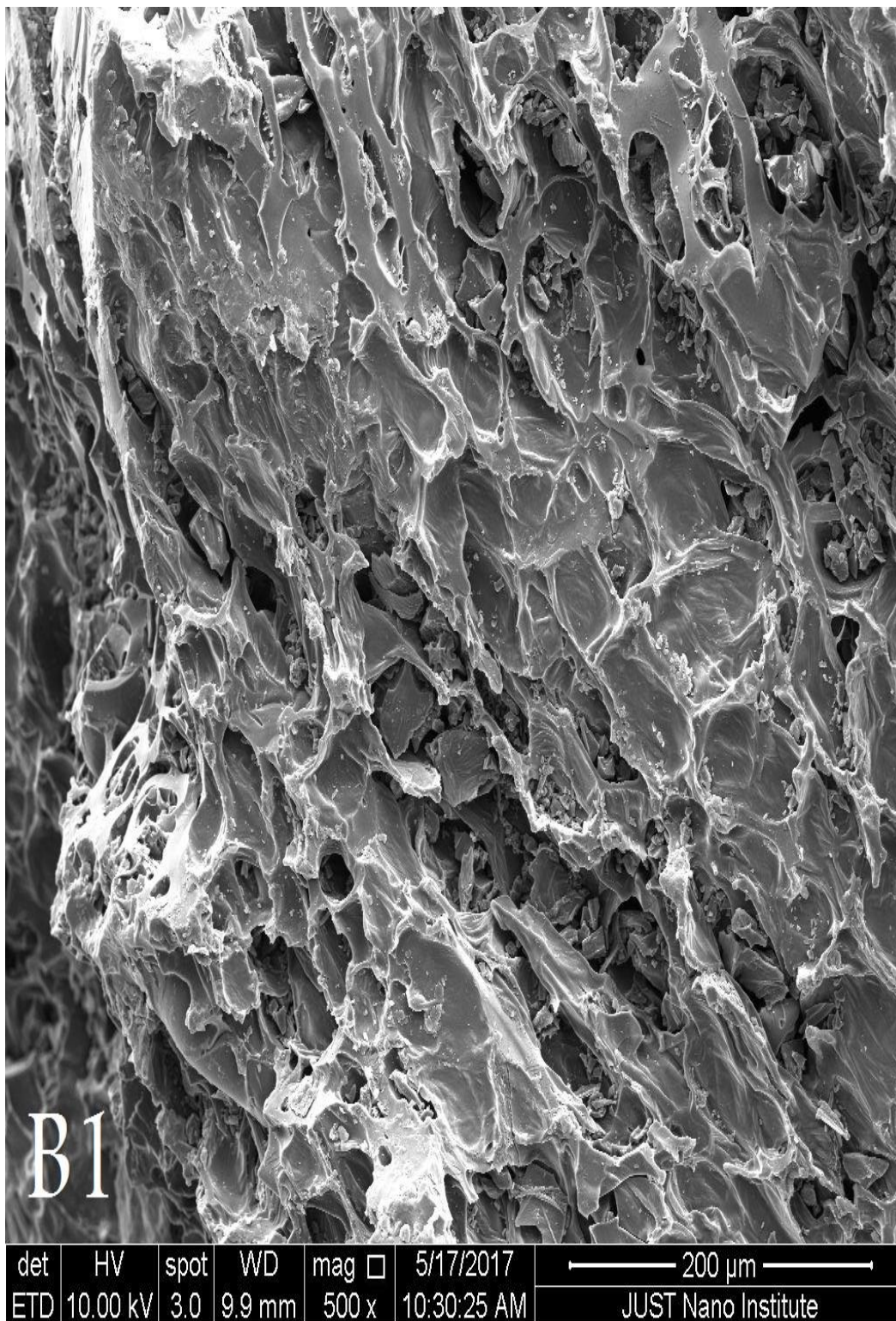
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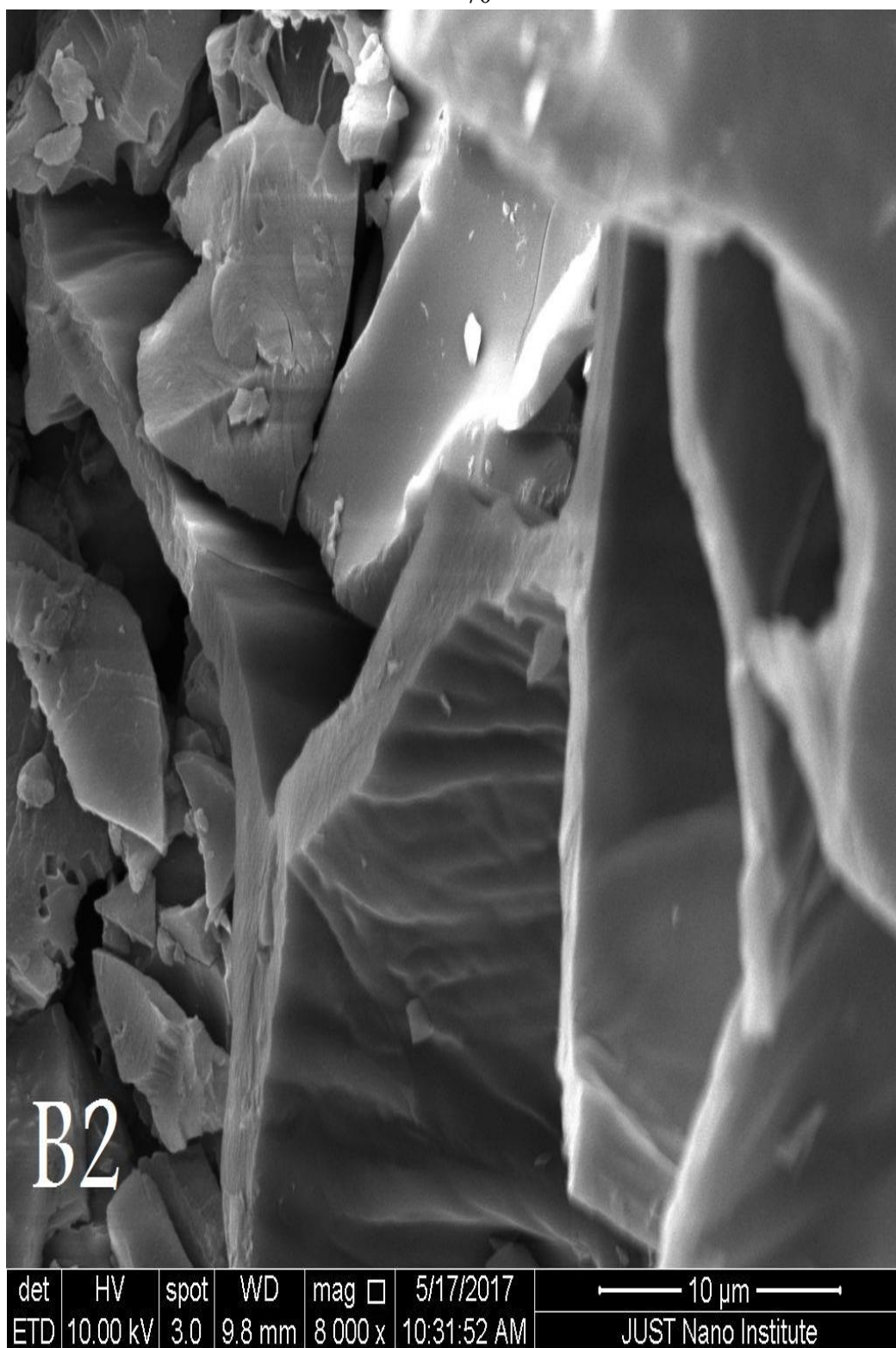
Appendix 1

SEM micrographs for the *Cupressus sempervirens* and *P. halepensis*
prepared activated carbon adsorption Cu, Ni ions

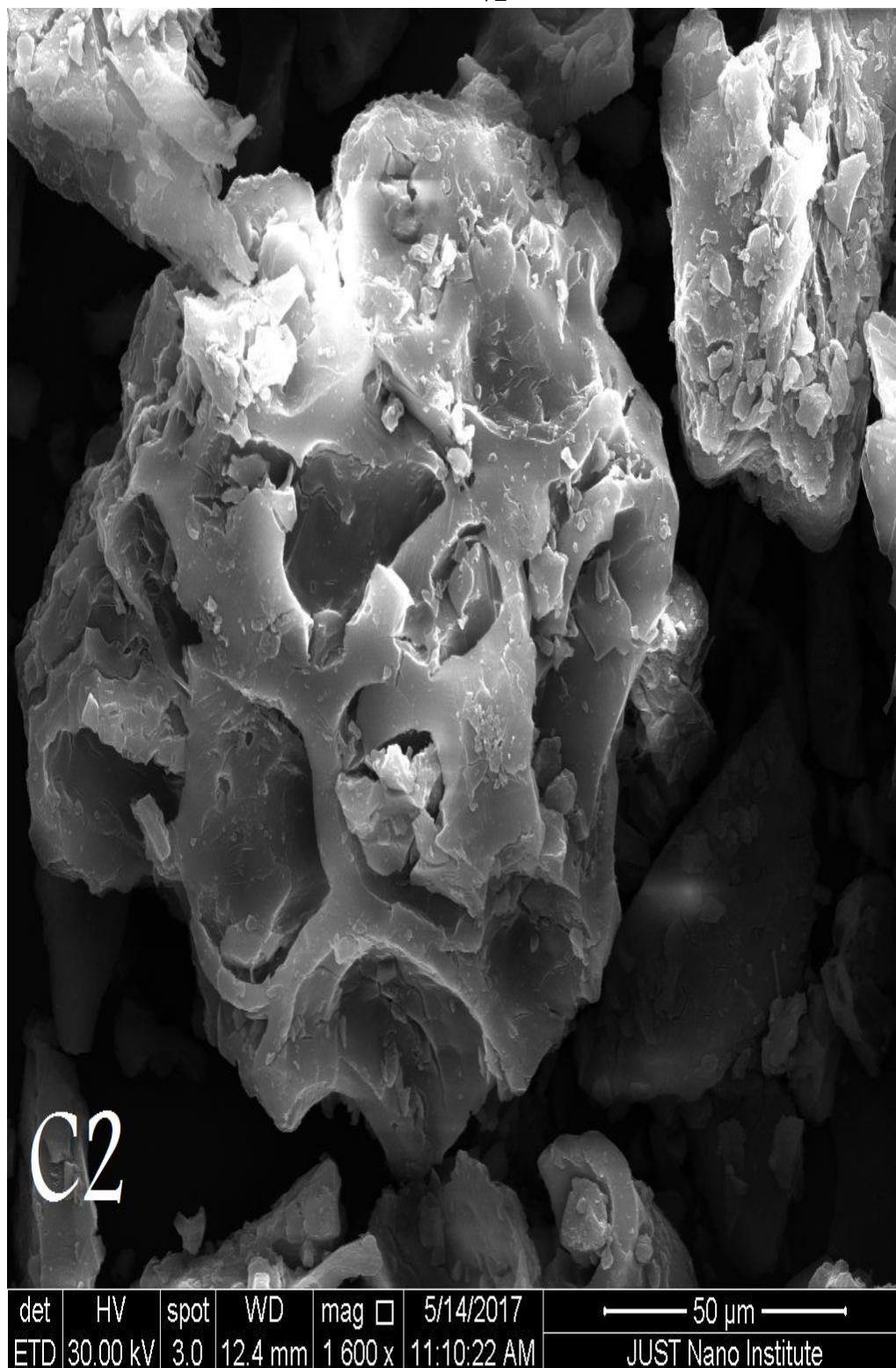


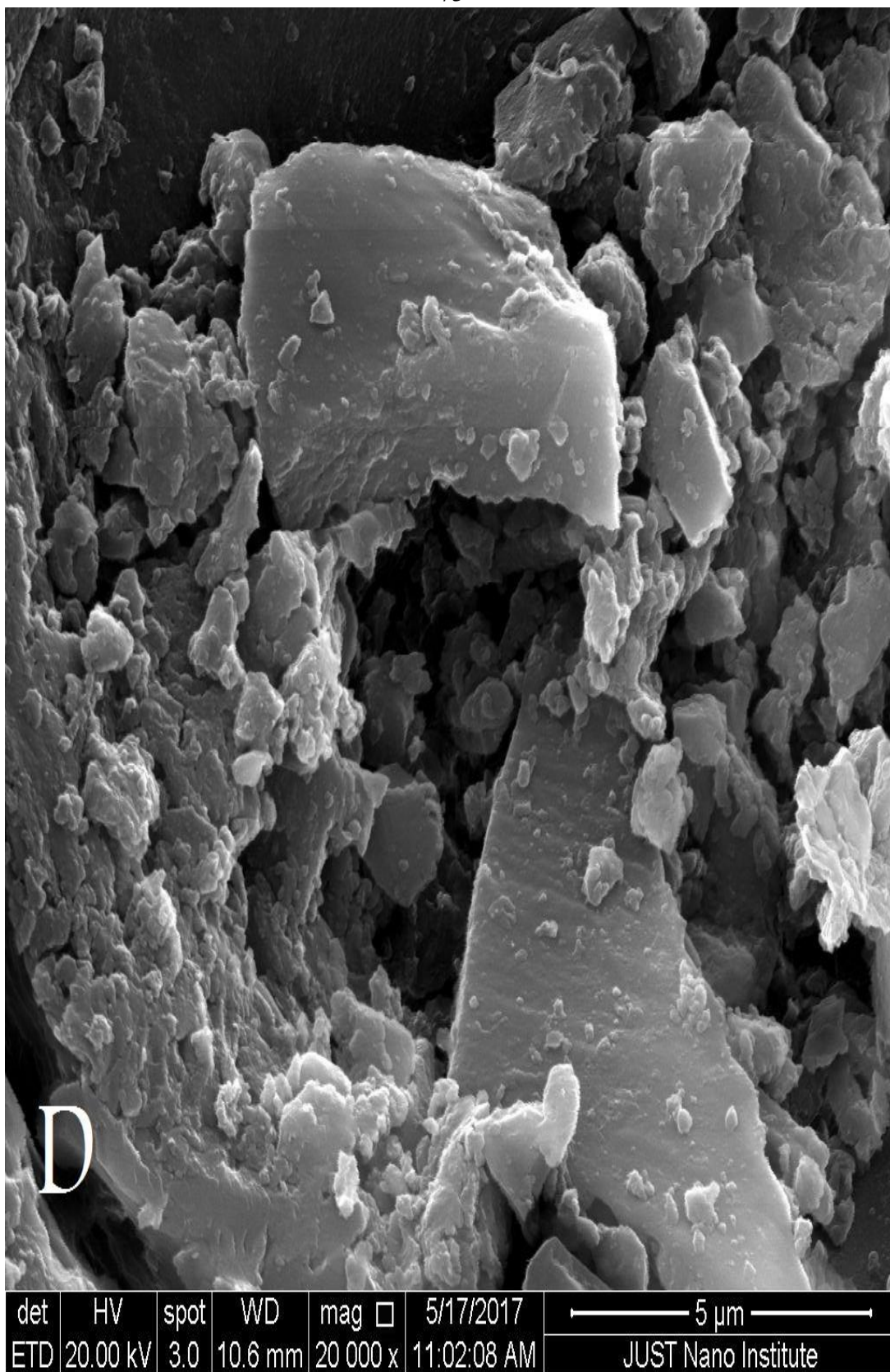


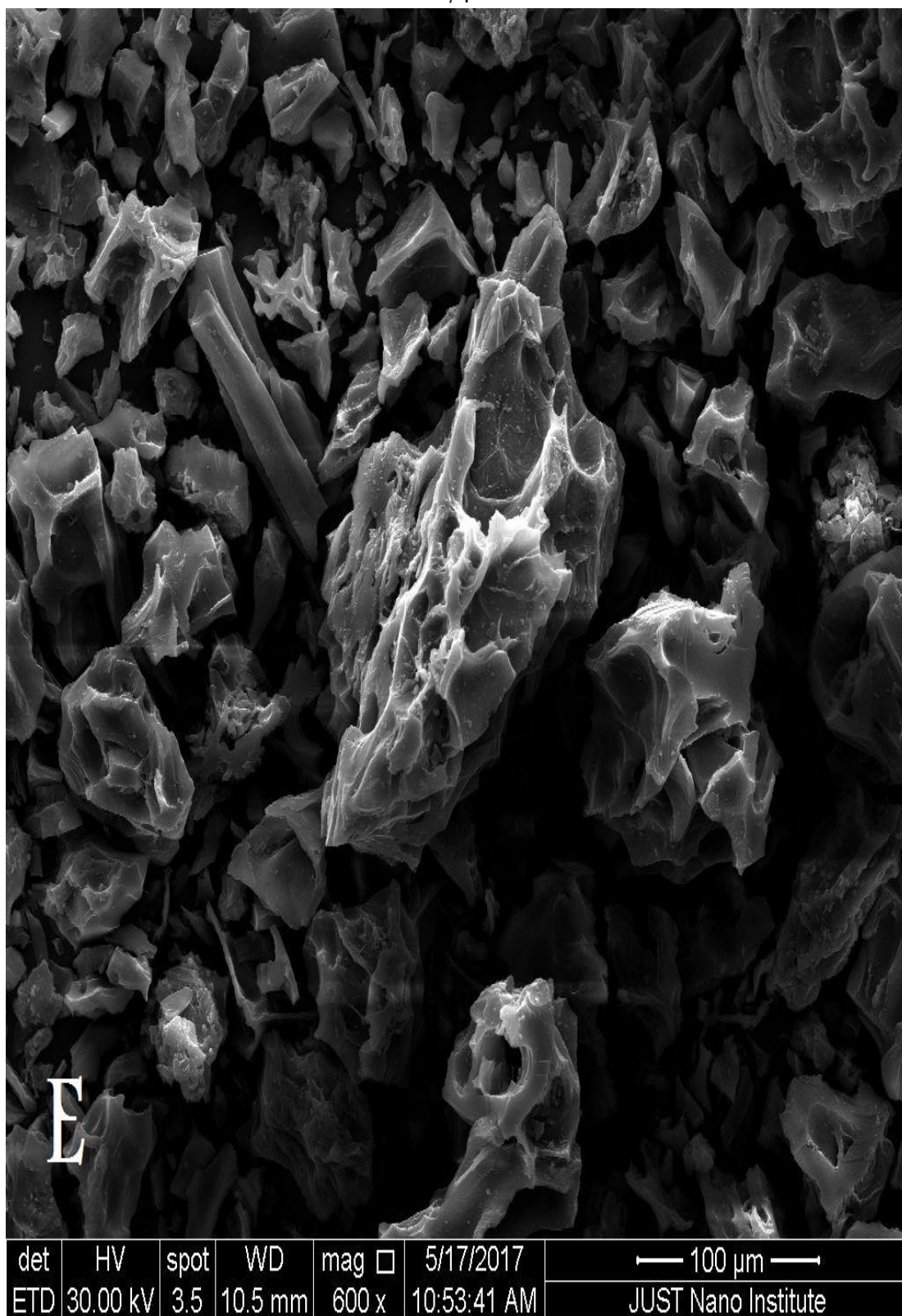


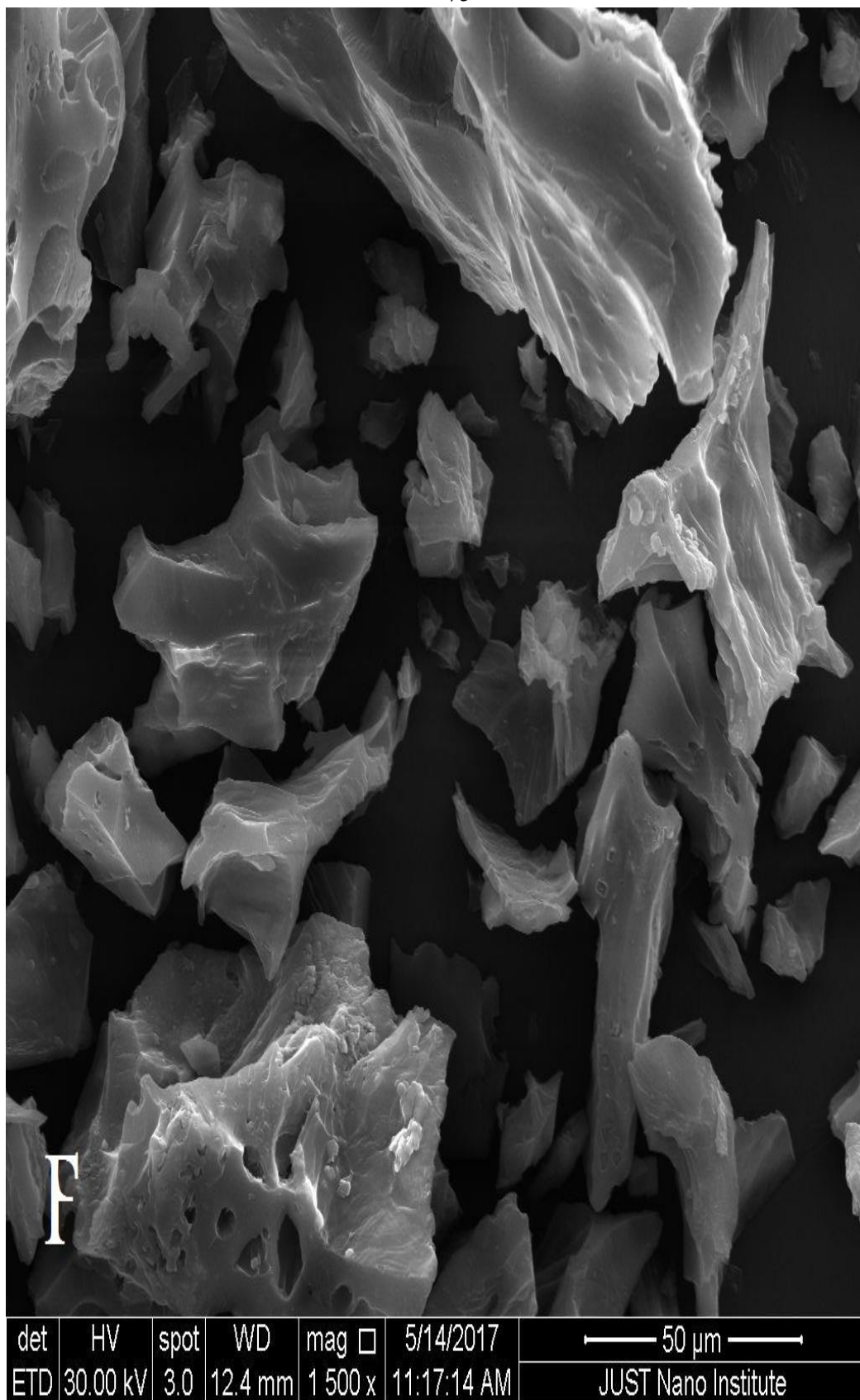






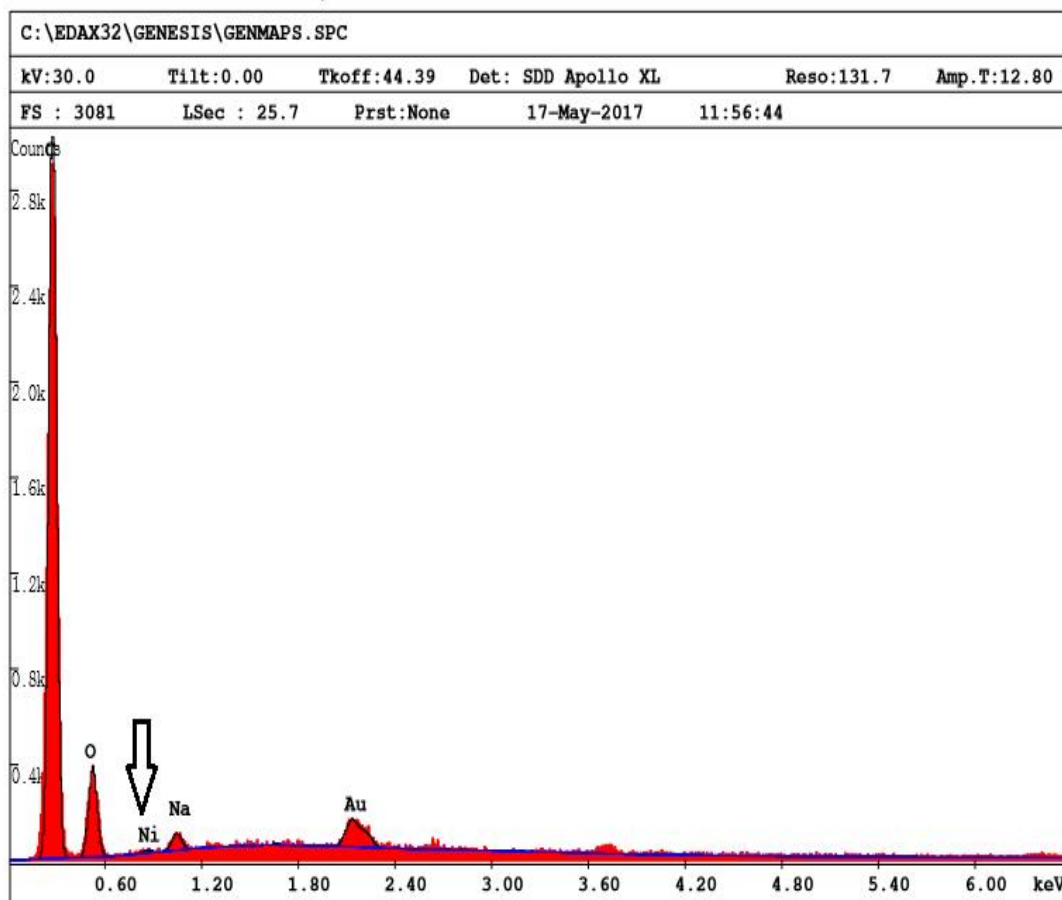
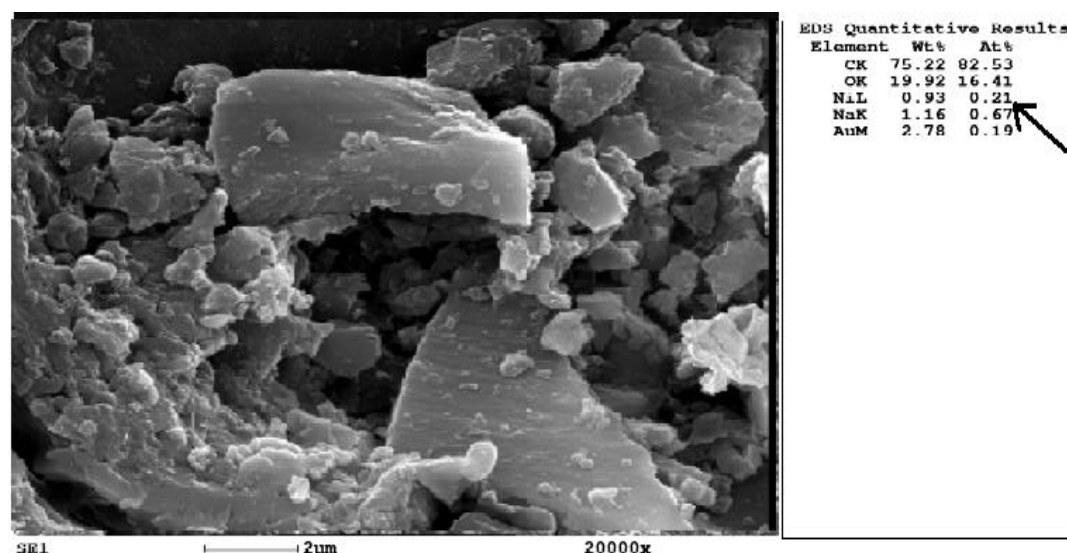


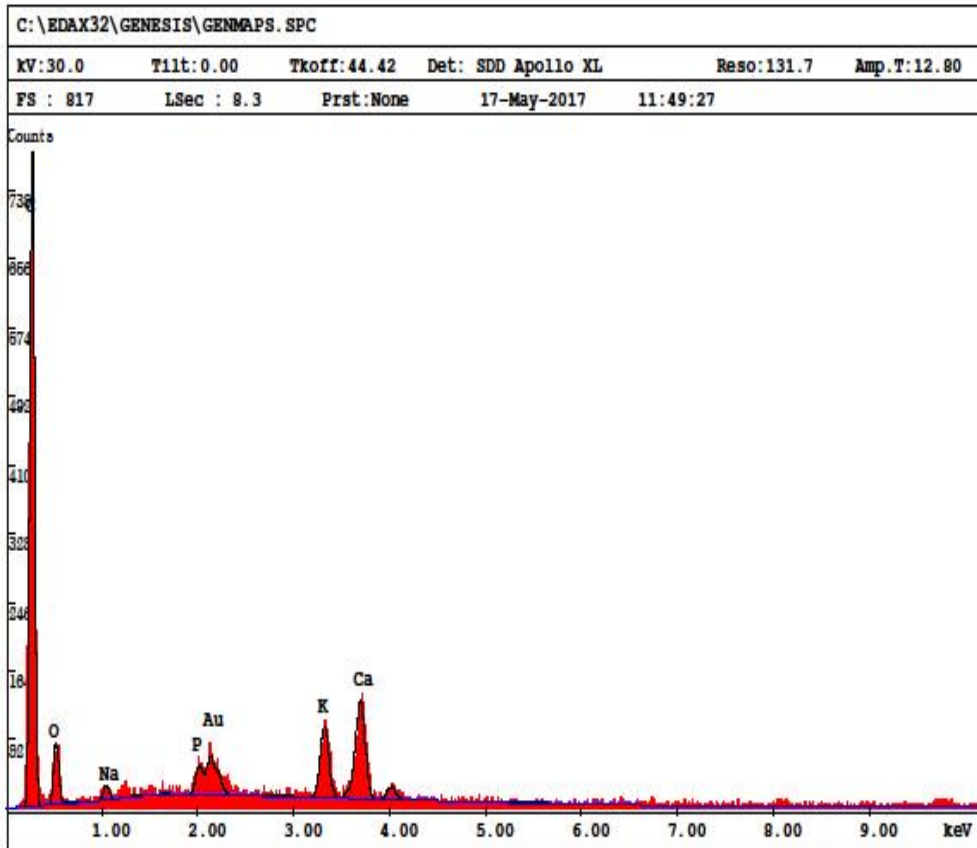
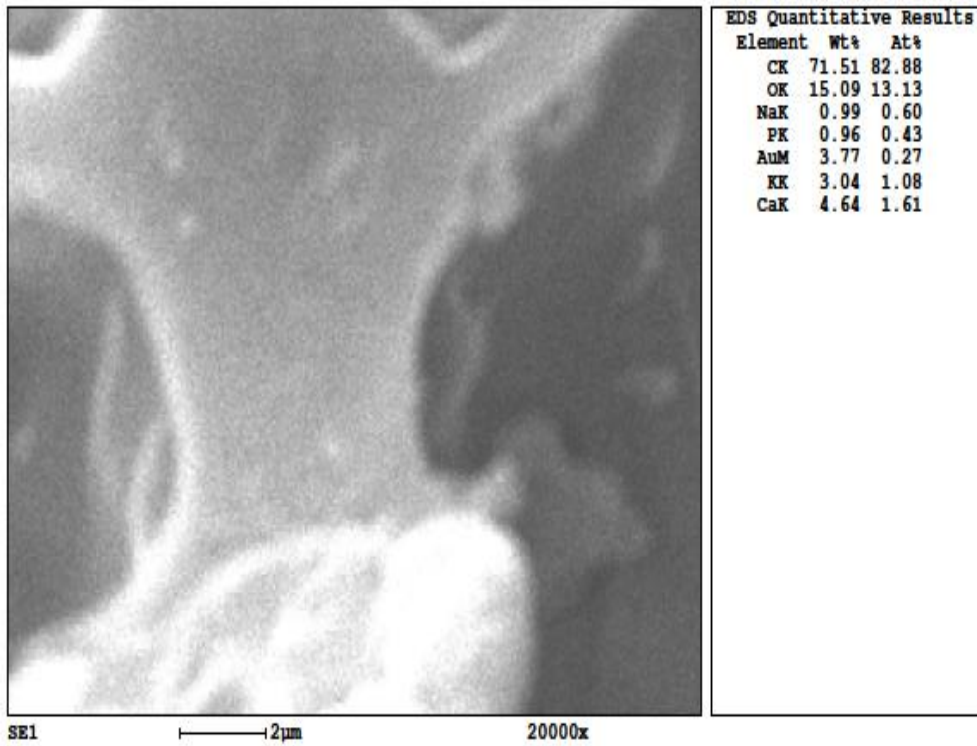


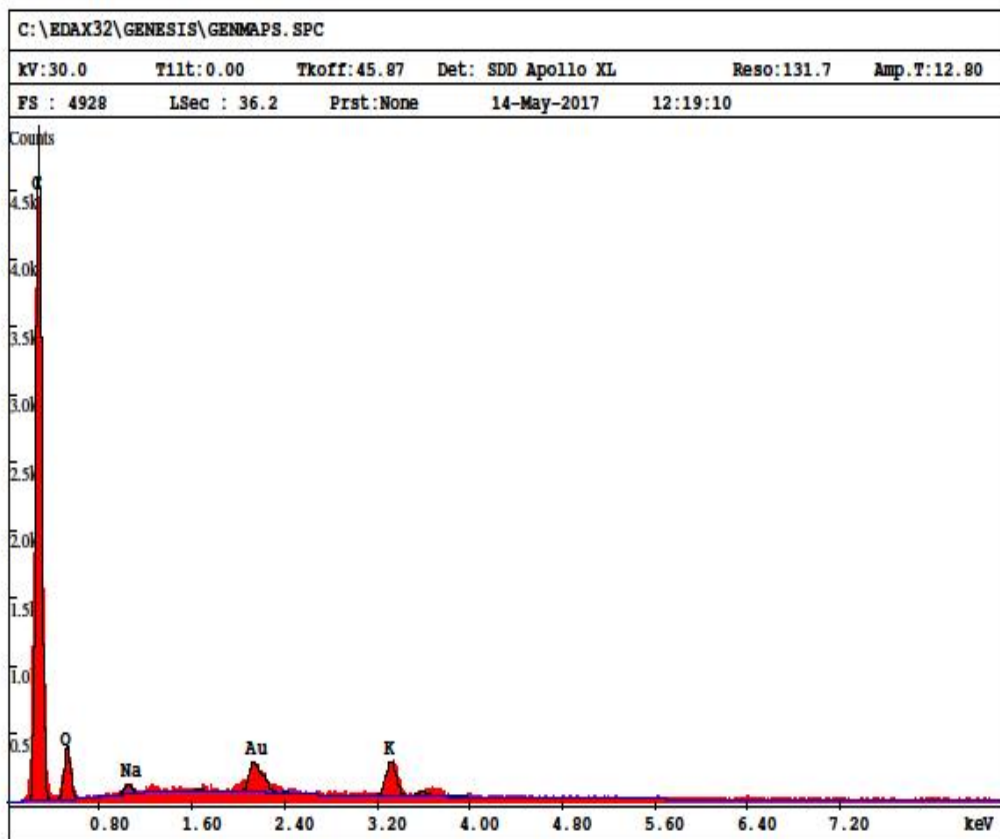
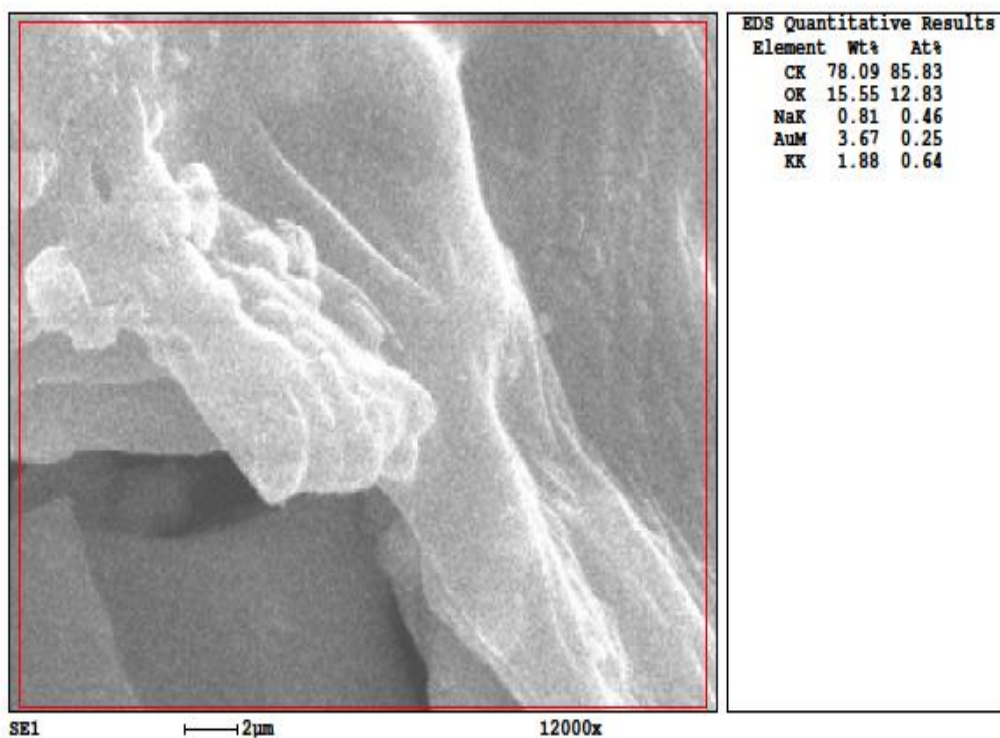


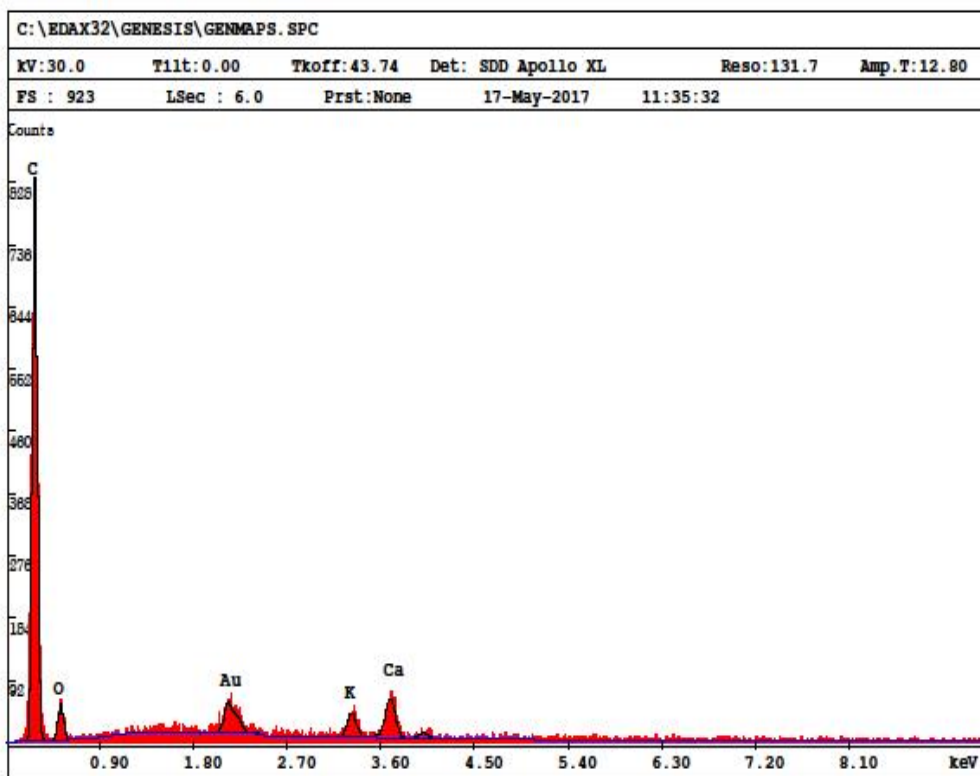
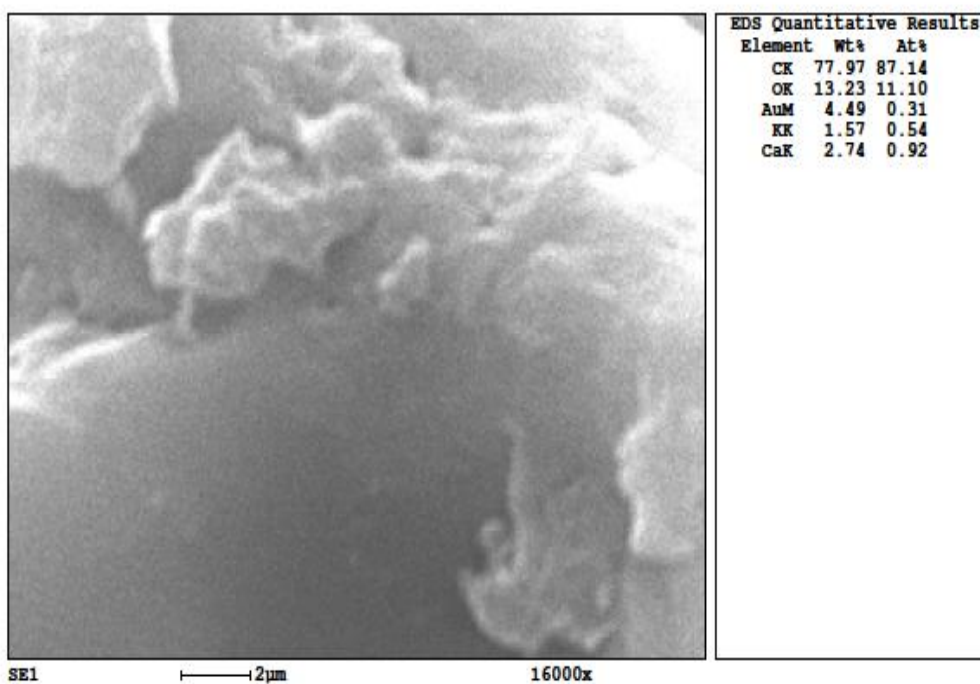
Appendix 2

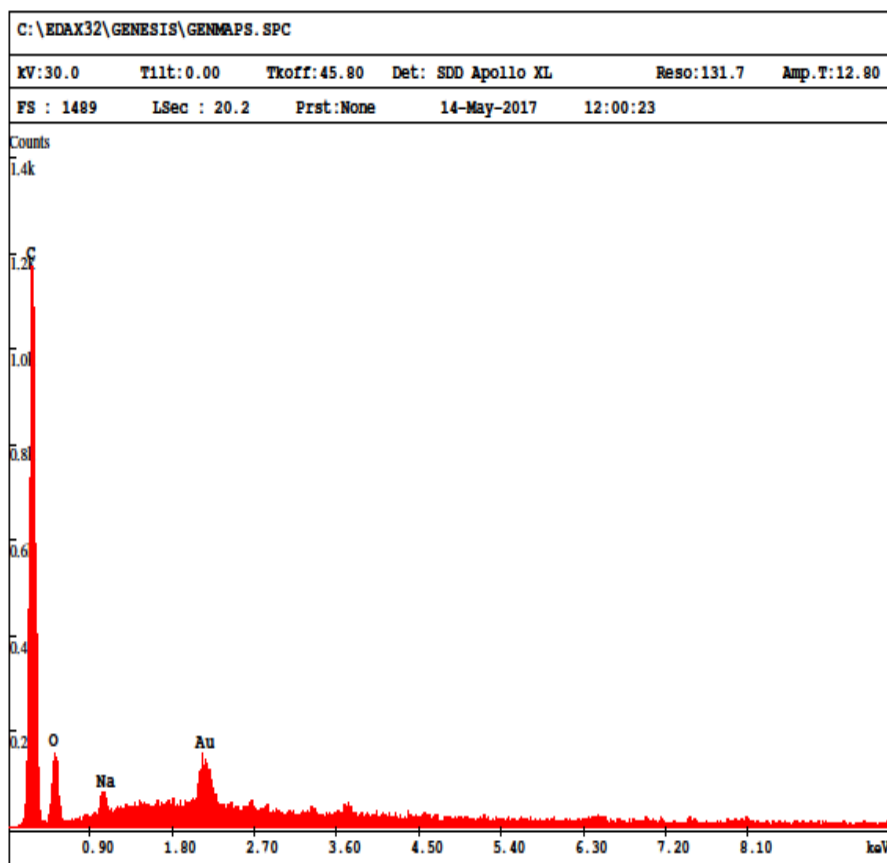
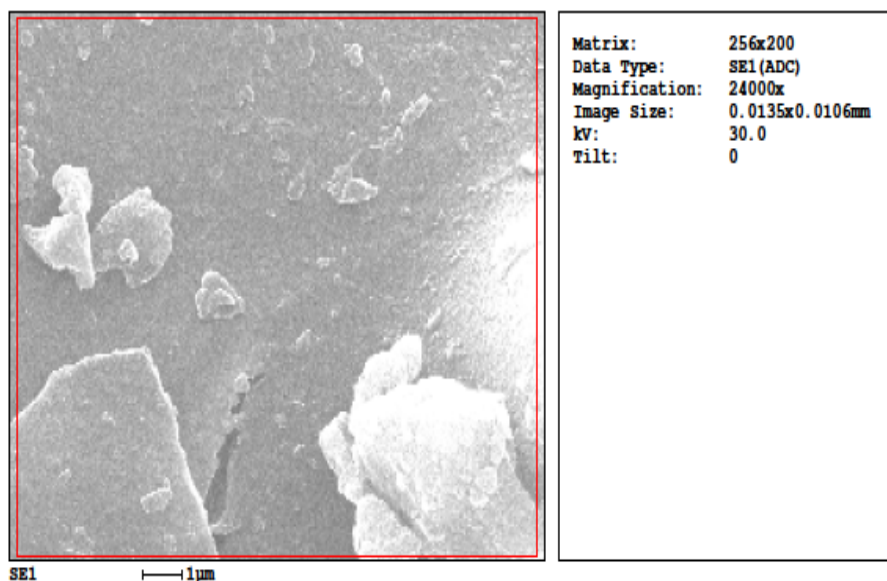
**EDX analysis for the *Cupressus sempervirens* and *P.halepensis*
prepared activated carbon adsorption: pure, with Ni, with Cu**

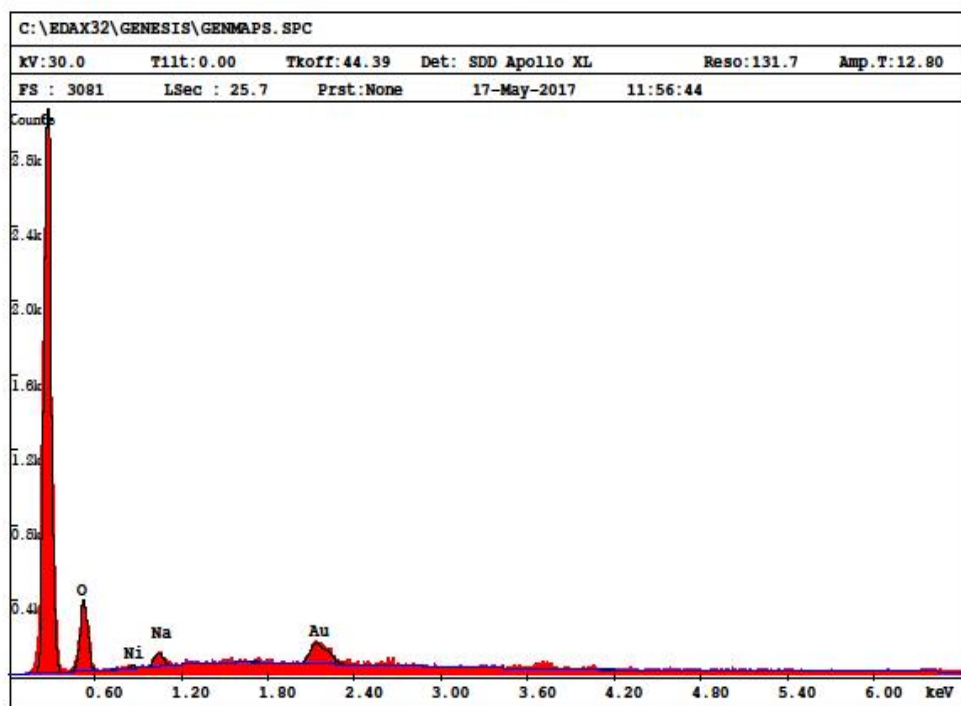
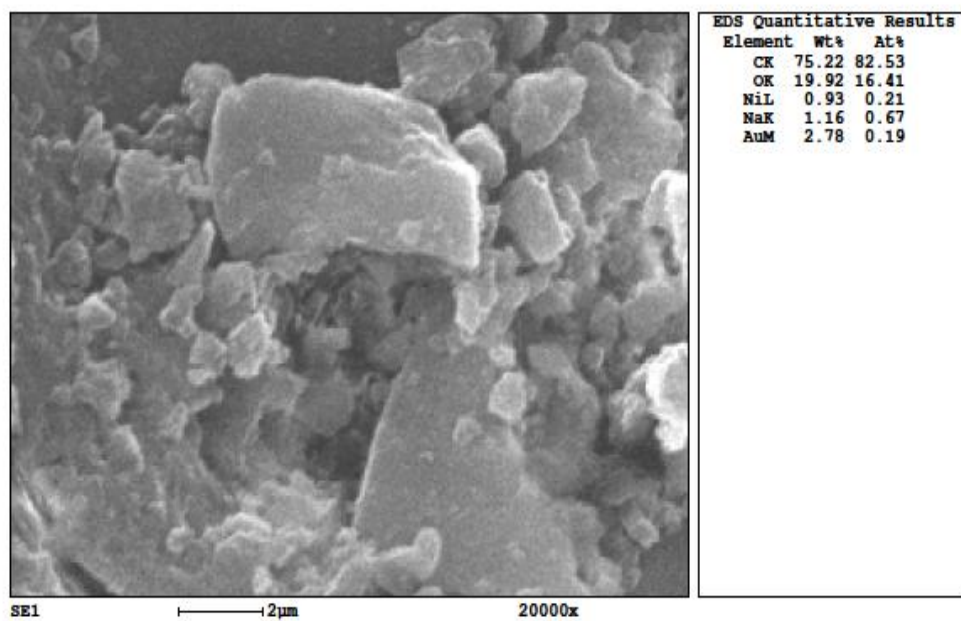












الفحص الكيميائي النباتي وإدمصاص أيونات النحاس و النيكل من
المحلول المائي باستخدام الكربون المنشط المستخلص من ثمار
السرو والصنوبر

إعداد
روان رائد جمال عتيق

إشراف
د. أحمد أبو عبيد
د. نضال جرادات

قدمت هذه الأطروحة اكتمالا لمتطلبات الحصول على درجة الماجستير في العلوم البيئية بكلية
الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين .

ب

الفحص الكيميائي النباتي وإدمصاص أيونات (النحاس، النيكل) من المحلول المائي باستخدام الكربون المنشط المستخلص من ثمار السرو والصنوبر

إعداد

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د. نضال جرادات

الملخص

لمحة عامة:

تعتبر أيونات العناصر الثقيلة سامة وخطرة للبيئة وذلك بسبب تراكمها في أجسام الكائنات الحية وانتقالها إلى المياه الجوفية. التلوث بالنحاس والنيكل يعتبر من أخطر العناصر الثقيلة بسبب الاستخدام المفرط لها بالصناعات مثل التعدين والتجسيم، مصانع الطلاء، واستخدامها في الأسمدة والمبيدات. إن التراكيز العالية من هذه العناصر تسبب سمية للكائنات الحية وكذلك العديد من الأمراض الحادة والمزمنة بالإضافة إلى سرطان العظام والرئة. هناك عدة طرق لإزالة وتنقية هذه العناصر من المحاليل المائية، أكثرها فاعلية وأقلها كلفة استخدام الكربون المنشط وهو ما تم اعتماده في هذه الدراسة.

الأهداف:

إزالة العناصر الثقيلة من المحاليل المائية باستخدام إدمصاص الكربون المنشط المحضر من ثمار السرو والصنوبر، بالإضافة لعمل اختبارات على الزيوت الطيارة لهذه النباتات، لفحص مضادات الأكسدة في فلسطين، ومقارنة النتائج بعدة مناطق في فلسطين.

الطريقة:

تم جمع عينات ثمار السرو والصنوبر من ثلاث مناطق مختلفة في فلسطين (الشمال والجنوب والوسط)، تجربة الإدمصاص شملت طريقة فيزيائية وكيميائية بالإضافة إلى دراسة عدة متغيرات

ج

شملت : التركيز، درجة الحموضة، الوقت، الحرارة واختلاف كمية الكربون المنشط في المحلول المائي. فحص اليود والمجهر الالكتروني الماسح تم دراستهم لتدعيم هذه الدراسة. تم اعتماد طريقة DPPH لتحليل مضادات الأكسدة باستخدام جهاز التحليل الطيفي واستخراج الزيوت الطيارة باستخدام جهاز الميكرويف.

النتائج:

تم حساب نسبة إدمصاص عناصر النحاس والنيكل من ثمار السرو والصنوبر باستخدام جهاز AAS، تفوقت على نتائج الفحم التجاري، حيث كانت نسبة إزالة أيونات النحاس من المحلول المائي 99.9% باستخدام السرو، والنيكل 99.6% لنفس النبتة. أما فيما يتعلق بالكربون المنشط المستخرج من ثمار الصنوبر، كانت نسبة إزالة أيونات النحاس 99.1% وأيونات النيكل 98.5%. مساحة السطح باستخدام فحص اليود كانت 726 م² غرام، للسرو و 1257.3 م² غرام للصنوبر. تم تفسير نتائج عملية الإدمصاص التي تم الحصول عليها عند الاتزان باستخدام معادلة لانجمير وفرينليش، حيث كان نموذج فرنليش أنسب لتفسير إدمصاص النحاس والنيكل عند 25 درجة مئوية. أما فيما يتعلق بمضادات الأكسدة كان السرو أعلى مضاد للأكسدة بجنوب فلسطين في حين الصنوبر أعطى نتائج مضادة للأكسدة في شمال فلسطين.

الاستنتاج:

من نتائج هذه الدراسة توصلنا إلى أن السرو والصنوبر يمكن استخدامهما لإزالة العناصر الثقيلة من المحلول المائي باستخدام الكربون المنشط ، كذلك يمكن استخدام أجزاء أخرى من هذه النباتات، لتكون بديل طبيعي عن الفحم التجاري، ويمكن عمل دراسات طبية للبحث في مجال الزيوت الطبيعية ومضادات الأكسدة لهذه النباتات.