**An-Najah National University**

**Faculty of Graduate Studies**

# OLIVE INDUSTRY SOLID WASTE WITH IONIC FUNCTIONALITY: PREPARATION, THERMAL BONDING AND USE AS A METAL ADSORBENT FROM WASTEWATER

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**This Thesis\Dissertation is Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Chemistry, Faculty of Graduate Studies, An-Najah National University, Nablus - Palestine.**

**2022**

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This thesis was defended successfully 0n
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# Dedication

I dedicate my thesis to my beloved, supportive family, my soulmate husband Fadi, my dear princesses (Razan and Mera). Thank you for your help, patience and cooperation.

I also dedicate it to my loving, caring mother and great, supportive father, wishing them both long lives and good health, as well as my beloved brothers Ahmad, Akram, and Basheer and my precious sisters, Ahlam and Fairouz.

also, to my second family, my husband's family, my beloved five sisters in low, to my Aunt, and to the soul of my father in low may he rest in peace.

I also dedicate it to my Grandma's soul, Which I will never forget.

I also dedicate it to all my teachers who never failed to supply me with vital information during my studies. Finally, I would like to thank everyone who has helped, supported, and encouragement me throughout my studies, Even if with a word.

# Acknowledgment

First of all, I would like to thank our Great, Merciful God, for letting me through all the difficulties. I have experienced your guidance day by day. I will keep on trusting you forever.

I would like to express my sincere gratitude to my great advisor Prof.Othman Hamed for his continuous support, patience, motivation, enthusiasm, and immense knowledge. His guidance, Notes and directions helped me during my study, I'm so glad to have a scientist like him as my supervisor.

A special thanks and appreciation for my Co-Supervisor Dr. Hisham Qararya for his great support and continuous Follow-up with my research and thesis step by step, thank you for your time and knowledge.

This master degree was a dream to me, but I was not able to earn it without help, Guidance, educations, and assistance from the chemistry department at

Al-Najah national university represented by chairman of the department and lecturers' doctors, and laboratory technician.

There is no doubt that the presence of good friends was one of the most important reasons for overcoming all difficulties, so they deserve a lot more than thanks, I've been through hard days, but the Presence of good friends I got to know them from the master classes, made it easy for me to pass, thank you for always being there for me Reem, Haneen, Raneem, and Jomana. Wish you all the best in each step of your lives.

Also, I would like to thank chemistry department staff at Arab American University for their support, thanks dear Doctors and coworkers' friends.

Finally, I would like to thank myself for my courage to continue my education after a long time of graduation, with all of my responsibilities.

# Declaration

I, the undersigned, declare that I submitted the thesis entitled:

**OLIVE INDUSTRY SOLID WASTE WITH IONIC FUNCTIONALITY: PREPARATION, THERMAL BONDING AND USE AS A METAL ADSORPENT FROM WASTEWATER**

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

**Student's Name:** _____

**Signature:** _____

**Date:** _____

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**OLIVE INDUSTRY SOLID WASTE WITH IONIC FUNCTIONALITY: PREPARATION, THERMAL BONDING AND USE AS A METAL ADSORPENT FROM WASTEWATER**

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## Abstract

**Background**: The most important resource for life's survival is water. Unfortunately, Due to the fast growth of population, increase global industrial activities, careless utilization of natural resources, water pollution crosses the limits. Contaminated water with hazard's heavy metals from industrial and agricultural sources is one of the most critical issues that World Health Organization (WHO) and researchers focusing and searching for suitable solutions to eliminate it. Modifying existing polymers may be the simplest and most productive way to develop a low-cost adsorbent with high efficiency against metals and hazardous organic compounds.

**Objectives**: The purpose of this study was to establish a natural source and low-cost technique to make a new adsorbent for hazardous metal ions. What distinguish our study is the use of a raw natural polymeric materials, usually a commercial polymer used at other studies.

**Methodology**: Adding carboxylate functionality to Olive Industry Solid Waste (OISW) components (cellulose, hemicellulose, and lignin) by CMC reaction, after subjecting the waste to purification by Soxhlet extraction, followed by thermal treatment produced

Carboxymethylated OISW polymer a novel polymer with new ionic functionality.

**Results:** The polymer was characterized using FT-IR, TGA, and AFM, to examine the polymers structures and its thermal stability, and to obtain a Nano scale image of the polymer surface respectively. Degree of substitution and solubility of the produced polymer were also determined.

Carboxymethylated OISW polymer was tested as a Pb(II) and Cu (II) ions adsorbent that were used as model ions in this study. Metal ion concentration, temperature, pH, adsorbent dosage contact time and shaking speed were all evaluated as parameters influencing the adsorption process. The percentage removal of Pb(II) by carboxymethylated OISW polymer was about 85 percent rate, and that of Cu(II) was 93 percent.

Adsorption isotherm, kinetics, and thermodynamics were also investigated in order to obtain a better knowledge of adsorption spontaneity and mechanism. As determined by the adsorption parameters, Langmuir isotherm of adsorption, and Freundlich isotherm model was tested. Equilibrium reaction with Cu(II) obey Langmuir isotherm model, and pseudo-second order reaction, also for Pb(II) results shows that Langmuir isotherm model obey, and pursues a pseudo-second order model. Also, the reaction thermodynamics indicates that the adsorption process is spontaneous.

**Conclusion:** Adsorption efficiency of the Carboxymethylated OISW polymer was evaluated on a real-wastewater (sewage) sample as well. The polymer showed quantitative removal for most of the toxic metal ions present in wastewater not just lead and mercury.

**Keywords:**

Carboxymethylated OISW polymer; Copper; Heavy metal; Lead; Olive industry solid waste; Water pollution, Water treatment,

# Chapter One
# Introduction

## 1.1 Preface

Our planet earth consists of two areas, 29.00% land areas, 71.00% water areas. Oceans and seas contain 97.60 % of the planet's water, which is salty and not healthy for drinking. And the remained 3.00 % is drinkable that comes from a limited number of sources including lakes, rivers, streams, and underground water [1]. Water is an essential resource and the most important for survival of life on Earth. Clean water is vital for humans, animals, plants and other organisms. 60.0-75.0 % of human body weight is water [1], so it is the source of living. The importance of water not limited for drinking or household needs, it is also required for several products to be prepared and synthesized. Similarly, water is used in the production of many food products. Briefly the block of the world's agriculture, industry, and electricity is water. The world currently facing two major issues about water, first, irresponsible use of natural resources of water and excessive consumption of water. Second, water distinguished by the capability of dissolving a wide range of inorganic and organic components, which makes it significant in many necessary industries, but this feature unfortunately allows pollutants, hazards, chemicals, heavy metal to dissolved in our clean water and contaminated it [2].

## 1.2 water Pollution

The release of pollutants into subsurface groundwater, streams, lakes, rivers, estuaries, and oceans is defined as water pollution, in addition to release of substances, such as chemicals, organics, heavy metals to the stage where the compounds interact with useful water use or the ecosystems' natural functioning [3]. Due to the fast growth of population, increase global industrial activities, careless utilization of natural resources, water pollution cross the limits. Different sources of pollutants come from insecticide, herbicides, factories, sewage water, fertilizers, pesticides such as organic waste, chemicals and toxic heavy metals, these become the primary sources of water pollution [4]. Water pollution dilemma caused a serious environmental issue. As heavy metals amounts entering water sources, this increases massive toxic problems in humans, animals, organisms [5, 6].

Water pollution is one of the major concerns that researchers must address in the twenty-first century in enhancing water quality and reduce the impacts on human and environmental health [2].

### 1.3 Heavy Metals

Each and every hazardous metal, irrespectively of atomic mass or density, is a member of an ill-defined subcategory of elements that have metallic properties, can be classified as a heavy metal. Transition metals, metalloids, lanthanides, and actinides are among them [2]. Cadmium (Cd), mercury (Hg), Lead (Pb), arsenic (As), chromium (Cr), selenium (Se), nickel (Ni), copper (Cu), silver (Ag), and zinc (Zn) are examples of heavy metals. At the other hand Cesium (Cs), Aluminum (Al), manganese (Mn), cobalt (Co), strontium (Sr), molybdenum (Mo), and uranium (U) are some of the heavy metals are less common metallic contaminants [7]. Every metal species can be classified a "contaminant" if it took place in an unfavorable environment, or in a form or concentration that has a negative impact on humans or the ecosystem [7]. At higher concentrations, all metals are extremely toxic, and massive quantities can be hazardous to the body. Other toxic heavy metals include Plutonium, mercury and lead with no fundamental essential or desirable impact on organisms, as well as their concentration in the cells over time can result in serious disorder [7]. Heavy metals accumulation will destroy the human body's main metabolic process, as in case of arsenic (As), mercury (Hg), cadmium (Cd), and nickel (Ni) [8].

Heavy metal toxicity is based on a variety of factors, including the organism's exposure, the category of metal, its physiochemical rule, its character, and the period of time during which the organisms are exposed to metal.
For example, mercury concentrations above the allowable limit can affect neurobehavioral disorders, disorders of attention - deficit / hyperactivity, as well as mental retardation. Cadmium in large doses can affect bone damage, and a nephrotoxic effect [9-11]. Icterus, prostate cancer, liver cirrhosis, kidney damage, and anemia can all be influenced by zinc [12]. Arsenic generates melanosis, vomiting, skin cancer, nerve inflammation, and muscle pain [13].

### 1.3.1 Lead

Lead element with symbol Pb, have highest atomic number of any stable element 82.00 atomic number, and 207.20 atomic mass. it is a heavy metal with a higher density than most other materials, silvery with a hint of blue color [14]. Lead is derived from both primary and secondary sources. Primary lead comes from mining process, whereas secondary lead comes from reused products like batteries and lead pipe work [14]. The significant characterization of lead that it possesses a low melting point, its flexible, moldable, soft, corrosion resistance, make it one of the most widely used metals, having wide variety industrial applications [15]. Lead has been mined, smelted, refined, manufactured, and recycled, also used in household items industry's like paints and fuel additives. Through these human activities, lead find his way to our air, soil, water with unacceptable concentration causing contamination, toxicity and lead exposure. Lead exposure causing poisoning to humans with different symptoms according to age. Newborns children exposed to lead before birth could be born too soon, have a lower weight at birth and a delayed growth rate, signs and symptoms of lead poisoning in children include developmental delay, learning difficulties, irritability, loss of appetite, weight loss, sluggishness and fatigue, abdominal pain, vomiting, constipation, hearing loss, seizures, eating things, such as paint chips, that aren't food (pica) [15]. Adults lead poisoning symptoms are joint and muscle pain, high blood pressure, difficulties with memory or concentration, abdominal pain, mood disorders, headache, reduced sperm count and abnormal sperm, stillbirth or premature birth in pregnant women, miscarriage [15]. Lead has also been related to kidney problems, impaired cognition, disturbances in behavior, anemia and encephalopathy [9-11].

### 1.3.2 Copper

Copper (Cu) is a transition metal with atomic number of 29,00 and atomic mass of 63.50, a pinkish-orange color. It's one of the few metals exists in nature in a usable metallic form. Copper has a characteristic of conductivity to both heat and electricity that made copper useful in many industries. It is used in electrical apparatus such as motors and wiring, industrial operation like heat exchangers, construction (for example roofing and plumbing) [16]. As a trace mineral inside the nutrition, copper is required for every living thing, because it is an ingredient of the ventilatory enzyme system

cytochrome oxidase. It is also primarily found in the liver, muscle, and bone in humans [16].

human bodies cannot produce copper, but can have it from food especially animal sources. Copper levels in adults ranges between 1.40 and 2.10 mg per kilogram of body weight [17]. At copper concentrations of 3.00 ppm in blood and higher, symptoms of gastrointestinal poisoning appear [18], including Nausea and vomiting, abdominal pain, mucositis, and diarrhea, chemical hepatitis is distinguished by an increase in liver function enzymes [19]. High levels of copper in blood also cases anorexia, lethargy, and weakness [20].

### 1.4 Waste Water Purification and Adsorption Process

Since water is fundamental for living, and the consumption of water to cover the growing demands of anthropogenic activities and food preparation has been steadily rising, Recycling wastewater resulting from both human and industrial practices could be a realistic alternative to this demand [21] Since heavy metals enters our bodies and cause damages for organisms that we have shown and others through contaminated water with waste water from several industries, so that heavy metal ion removal from industrial waste waters has become critical for environmental pollution control before entering water sources. Reverse osmosis, membrane filtration, ion exchange, chemical precipitation, chemical coagulation, adsorption, and biosorption are several methods that have been developed for this purpose [22] . Most methods are inefficient, consume a lot of energy, provide poor removal efficiency, sensitive under certain operating conditions, generate hazardous waste sewage water require a lot of workforce, and are not financially viable [4]. So, adsorption method was discovered, it is a process of separation in which gas or liquid molecules bond towards outer and interior solid's surfaces object identified as the adsorbent, the separation depends on the selective adsorption of pollutants by an adsorbent kinetics, thermodynamic selectivity, due to direct interaction between both adsorbent surface and the adsorbed contaminants. Adsorption method features are availability, simplicity, practicability, profitability, low cost, cleanliness, eco friendliness, sorbent reusability, energy savings, small amount of sorbent required, less sludge generated, high efficiency and selectivity, easy to handle [4, 23].

There are two kinds of adsorptions. Adsorption by physical means which takes place when the adsorbate adheres to the adsorbent's surface exclusively through Van der Waals (weak intermolecular) interactions. is typically quick and reversible this is due to the fact that the adsorbate and adsorbent weak bonds are formed during the physical adsorption process

making smoothly established and destroyed adsorption bonds [24]. On the other hand, adsorption that results from a chemical interaction among both adsorbed species and the adsorbent surface is known as chemical adsorption. A chemical adsorption procedure is typically irreversible and slow since it necessitates the establishment of strong bonds between the adsorbate and the adsorbent and can modify both the surface and chemical properties of the adsorbate [24].

### 1.5 Olive Industry Solid Waste (OISW)

In terms of tradition as well as wealth, olive oil industry is extremely important in Mediterranean communities, during the last two decades, the olive oil industry has grown rapidly, its global output has growth by 2015/2016 with 3000000.20 tons, compared to 1990/1991 with 1000000.40 tons, Because of the nutritional value and financial interest in this raw material, production keeps growing. The olive oil industry produces a large amount of highly polluting byproducts, known as olive industry liquid waste (OILW) with 56.00% of waste from an olive mill content, and approximately 44.00 percent of solid waste from the olive industry (OISW), based on the fruit's moisture and olive fraction composition, and even the extraction process. The first is a combination of vegetation olive water, and water added to help in oil separation during the extraction process, while the second is made up of seeds and pulp residual fractions. Those certain waste products are acidic and contained exceptionally significant biological and excessive amounts of hazardous polyphenol as well as high BOD readings for chemical oxygen concentration [25-27].

More accurately, global municipal solid waste (OISW) output is expected to be around 1300 million tons annually, it is expected that by 2025, production will have risen to 2200.00 million tons per year, with nearly 46.00% organic content, since these wastes contain valuable natural resources, a small portion of them can be used as raw materials in various industries. research indicates that Olive Industry Solid Waste (OISW) could

be considered an economic resource. They have been used effectively in a variety of applications including such direct combustion, soil amendment, and livestock feeding. furthermore, owing to their huge economic concern and the capacity to be converted into products used in biotechnology, pharmaceutical industries, agriculture and the food service industry. OMSW may be a low-cost origin of organic and inorganic molecules that can be collected, so the solid waste presents a waste disposal challenge for the olive mills as well as a concern for environmental because they present a major challenge. inefficiency and environmental concerns have restricted these use pathways, as a matter of fact,( OISW) has a high moisture content and a moderate oxygen content, which limits its heating value and increases technical constraints and environmental risks such as deposition, corrosion, and high polluting emissions, moreover, the chlorine content in OISW exceeded the tolerable limit (> 0.70 percent in the pulp fraction), at this rate, using it in soil amendments may contribute in phytotoxicity and soil acidification due to the formation of HCl. In the same context using OISW in combustion may result in the formation of highly toxic chemicals such as dioxins and furans, furthermore, by discarding of liquid waste.

or sale it at a minimal price toward other industry sectors, the olive business misses financial, in addition of that in some nations, typically OISW is consumed as well as left to decompose, liberating Carbon dioxide to the air. Industrialists face a major problem with olive industry waste as environmental standards rising trend. For all of these reasons, OISW characterization and valorization has emerged as an important research area aimed at protecting the environment through waste management and renewable energy research. The defy is to repurpose this solid leftovers to beneficial as well as inexpensive usable products [27, 28].

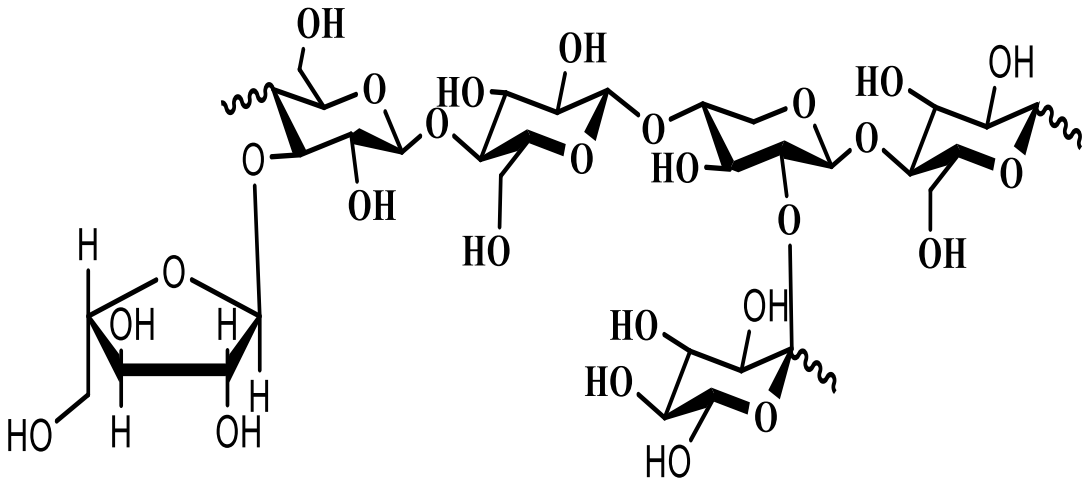
Olive industry solid waste is composed lignin, hemicellulose, and cellulose. Each repeat unit of the three macromolecules contains numerous hydroxyl groups, as have been previously shown in section 1.50, new water purification researches from heavy metals related to cellulose and modified cellulose. This work focuses on derivatizing OISW components by bonding an ionic functional group to the hydroxyl groups at (OISW) cellulose, hemicellulose, lignin and then thermally convert them to chemical bonded composites.

## 1.6 Hemicelluloses

Hemicelluloses is a branched polymer with the chemical formula $(C_5H_8O_4)_m$, where m reflect the degree of polymerization, it is a polysaccharides substantial part of the plant cell wall with the ability to form strong hydrogen bonds with cellulose microfibrils, also known as polyose. Hemicelluloses are not commercially valuable, as in case of cellulose. They are, however, an important topic because they can affect cellulose extraction and make significant contributions to wood and fiber quality. Hemicelluloses are composed primarily of xylose, glucose, mannose, galactose, arabinose, and glucuronic acid, with 0.80 atomic ratios between O/C and 1.60 for H/C. The hemicellulose content of OISW ranges from 14.40% to 36.58% of total weight. As shown in figure 1.1, hemicellulos have a several hydroxyl active site [27, 29].

**Figure 1.1**

*Structure of Hemicellulos*

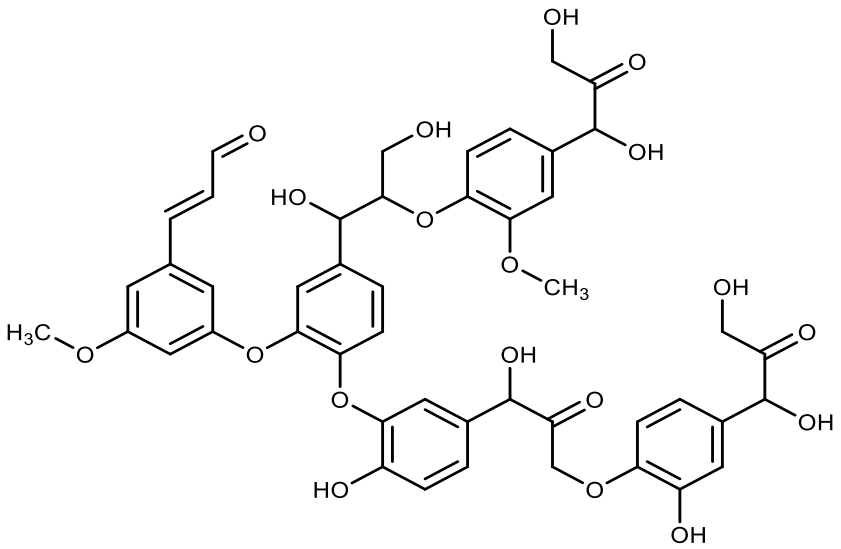


## 1.7 Lignin

Lignin, is a natural plant polymer made up of phenylpropanoid building blocks which are linked together by a variety of chemical cross bonding, forming a three-dimensional structure, its atomic O/C and H/C ratios varies between 0.47-0.36 and 1.19-1.53, respectively. It exists in all plants, a fundamental component and the second greatest commonly found organic building blocks upon cellulose on the globe. That reinforces, rigidifies, in addition to shapes plant tissues, is also regarded as an important microbial defense mechanism, and can prevent water from destroying plant cells' polysaccharide-protein sequence. It has the majority of methoxyl content in wood, it resists acid-hydrolyses, easily oxidized, soluble in hot alkaline and bisulfite, and easily condensed with phenols or thiols. Many efforts have been made to specify lignin or lignin based on their composition, structural characteristics, and formation mechanism. The lignin fraction in OISW ranges from 20.30% to 43.20% according to recent literatures [27-30]. As figure 1.2 shows, lignin has a lot of hydroxyl, carbonyl, and ether active sites that allow addition new active functional groups to serves our purpose adsorption heavy metals from waste water.

**Figure 1.2**

*Lignin Structure*

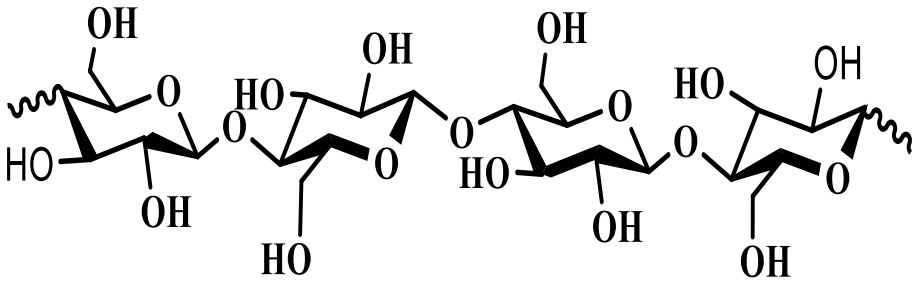


## 1.8 Cellulose

Cellulose, a polysaccharide or a carbohydrate organic complex, with chemical formula $(C_6H_{10}O_5)$ m, with 162.14 g/mol molar mass per glucose unit. This linear glucosan polymer, containing at least 3,000 glucose units made up of a linear polymer of hundreds to thousands of (14) linked D-glucose items [26].

**Figure 1.3**

*Molecular structure of cellulose*




The most fundamental plant cell wall structural element, Cellulose contributes to roughly 33.00percent among all vegetable matter (cellulose accounts for 90.00% cotton and 50.00% wood) and it is the greatest abundant species of all organic molecules. Cellulose is not digestible by humans but it considered a source of nutrition for herbivorous animals. Numerous industries are manufactured from cellulose as papers, and fiber, also it is chemically altered in order to produce materials used in the manufacture of plastics, photo and video films, and natural fibers. Some cellulose compounds are employed in the manufacture of adhesives, explosives, nutrition thickening agents, and humidity surface coating [31].

Cellulose has both crystalline and amorphous regions, the crystalline structure is preserved by Van der Waals and hydrogen bonds forces, twists and torsions in an amorphous structure change the ordered arrangement. Cellulose crystallinity and cellulose content are two of the most important microstructural parameters influencing natural plant fiber mechanical properties. All other components are significantly less stiff than crystalline cellulose, when using plant fibers as reinforcement in structural applications, it is essential to select plant fibers with a large cellulose content and crystallinity [32] .

Cellulose is very stable polymer, has high strength, density of about 1.5 g/cm$^3$ and decomposes at 260-270°C. It is characterized as water insoluble and insoluble in most organic solvents due to cellulose intermolecular hydrogen bonds among both hydroxyl groups and oxygen atoms chain, it's safe, has no taste no odor, chiral and biodegradable polymer [33].

The cellulose molecular structure has distinct characteristics including chirality, degradability, and hydrophilicity, and spacious high donor reactivity of the hydroxyl groups causes chemical variability. Each cellulose unit (figure 1.3) has three active hydroxyl groups that can undergo classic primary and secondary alcohols reactions. These properties make cellulose a good candidate for metal adsorbent and other applications [33, 34].

OISW cellulose content varies significantly between 24.10% and 36.60 % of its total weight. Furthermore, in comparison to pulp and residual olive cake, the olive pit has the highest cellulose content of OISW with average 35.00% cellulose content [34].

### 1.9 Related Research Using Cellulose

Recently, research in this area has focused on developing low-cost natural-based materials for commercial use. Numerous Synthetically produced cellulose materials were generated and applied to water treatment. The natural polymer that received good attention in this field of study is cellulose; especially chemical modification to cellulose polymer by addition of highly active different functional groups in order to improve the adsorption capacity [35, 36].

A study used cellulose and polyethylene loaded with glutaraldehyde to create microscopic spheres. This product was tested for its ability to remove Pb(II) ions from a solution containing various Pb(II) ions concentrations using isothermal calculations and kinetic models this product's capability to adsorb Pb(II) ions was discovered been nearly nine and a half mg/g, that further surpasses ability of cellulose microspheres that absorb approximately 50.00% [37].

Cellulose treated chemically with a methyl pendent Benz aniline, producing chelating units in one study. Copper(II) and lead(II) were removed from aqueous solution using

modified cellulose. Adsorptions kinetic characteristics match the pseudo-second-order kinetic model nicely [38].

Other researchers focused at cellulose and polyethylene amine microspheres. At first synthesized them and cross-linked them with glutar-aldehyde, based on adsorption kinetics and isotherm equations, cellulose microspheres were examining the efficiency of $Pb^{2+}$ removal out of contaminant solutions, furthermore, there research discovered that adsorption efficiency fit Freundlich isotherm equation and pseudo second order kinetics equation [39].

Another chemically modified cellulose adsorbent was synthesized using a Schiff base tertiary amine-chelating group in order to get rid of $Hg^{2+}$ hazardous ions from contaminated solution. In this study they discovered that the pseudo-second order kinetic model and the Langmuir isotherm were well suited for the adsorption of $Hg^{2+}$ ions from aqueous media [40].

Cellulose Ester was also employed for this aim; it was made by solid-state reaction of succinic anhydride and cellulose which is obtained from inexpensive filter paper.

The polymer were tested at the removal of Copper ions from polluted water at pH = 4.0-5.0, the cellulose ester removed 94.00% of the Copper ions at room temperature and 50.00 min mixing [41].

In other study, the data showed that thiosemicarbazide modified cellulose performed well as Hg(II) adsorbent of contaminated water, reaching an adsorption efficiency equal to 500 mg/g. Cellulose was tested as a Hg(II) adsorbent in polluted water. adsorption results were applied to the Langmuir model and the pseudo-second order kinetic model. $R_2$ (the fitting coefficient) close 1.0. The enhanced efficiency of thiosemicarbazide modified cellulose for Hg(II) was associated with the chelating interaction of Hg(II) and thiosemicarbazide [42].

As previous research shown, whenever converted into glucose or cellulose by chemical or enzymatic hydrolysis, is an important source of ethanol and an industrial raw material for a huge number of derivatives with an infinite number of commercial applications. Surface modified cellulose is also of great interest because of its numerous possible applications [43].

The recent research focused on used Raw materials like coconut fibers were used to extract cellulose in order to purify waste water with it, the adsorption of metals like $Cu^{2+}$ and phenols were studded, the removal percentage was high and reached 181.00 mg $g^{-1}$ [44].

Cellulose filter paper modified with ethylenediamine tetra acetic acid was prepared by esterifying the paper with EDTA dianhydride and used to remove various metal cations like $Ag^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Sn^{2+}$, and $Zn^{2+}$ with a removal efficiency of 90-95 %. The cellulose-EDTA material works at a wide pH range and can be used as a solid absorbent or a membrane in waste water treatment [45].

In this research, the raw material was used is olive industry solid waste which content cellulose, lignin, and hemicellulose. OISW is alternative solutions to this problem include value-added lignocellulosic composites made from industrial waste [25].

### 1.10 Related Research Using Olive Industry Solid Waste

In a study by O. Hamed Cellulosic material derived from olive industry solid waste was Characterized by FT-IR, XRD, and solid NMR spectroscopies, as well as FE-SEM microscopy, to check the structure of the generated cross-linked polymer cell-p-PDA after it was successfully hydrolyzed to nanocrystalline cellulose and cross-linked with a bidentate amine molecule. The cell-p-PDA polymer was tested for its ability to absorb the metal ions Pb(II) and Cu(II) from waste water.

At pH of 8.30 and at room temperature, it demonstrated great efficiency to adsorb both metals. similar to that Cell-p-PDA displayed great adsorption efficiency towards over 20.00 metals found in a real sewage water[21]. Another research olive industry solid waste (OISW) was used as a cellulose origin root. The Kraft pulping process was used to extract, and hydrolyzed with sulfuric acid to convert the extracted cellulose to cellulose nano crystalline. MNCs were synthesized by cellulose nanocrystalline reacting with $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$. Ability of these polymers (cellulose, NCs, and MNCs) to extract methylene blue (MB) from waste water was tested. Cellulose and NCs had an appropriate methylene blue inclination, whereas MNCs had amazing extraction efficiency [46].

### 1.11 Recent work of waste water purification using natural byproducts

Several researches have shown that rice husk which contains lignin could be used for removal hazardous metals from waste water. The highest adsorption capabilities ranged from 5.50 to 58.10 mg g-1. The removal efficiencies of nine different heavy metals using rice husk were investigated at a study, which showed that the removal efficiency raises in the following sequence Nickel (II)> Zinc (II)> Cadmium (II)> manganese (II) > Cobalt (II)> Copper (II)> Mercury (II)> Lead (II) [46]. In another study on the application of rice husks for adsorption of Hexavalent chromium, a huge noticeable removal more than 95.00% was reached at a pH of 3.00 as a result of Hexavalent chromium ions speciation at this low pH [47]. Another study using rice husks to remove Cu(II) it was found that a highest adsorption capability with 17.90 $mg.g^{-1}$[48]. Bansal et al., 2009 determined that rice husk had a maximum ability to absorb 8.50 mg. g-1 of Cr(VI) removal. They also discovered that treatment of rice husk with formaldehyde improved removal efficiency by nearly 23.00%[49]. Also research used phosphate-treated rice husk to extract Cd(II) from sewage water , discovered that it had a strong maximum adsorption capability of 103 mg g-1 at 20 °C [50].

Peanut residues which contains cellulose, hemicellulose, and lignin, discovered to function as ideal adsorbent for heavy metal removal, the extraction of Lead ions from sewage water using peanut shells reached the best adsorption capability of 39.00 $mg.g^{-1}$; at low pH levels, peanut shells were also found to be able minimize Cr(VI) reaching 4.30 mg.g-1 as highest adsorption capacity[52]. Furthermore, researchers successfully removed Cr(III) and Cu(II) adsorption capacities of 27.9 and 25.4 mg g-1 were achieved using peanut shells, respectively [53].

Peanut hull a common agricultural byproduct, was also demonstrated to extract Copper (II) ions, reached a highest adsorption capability with 21.30 mg $g^{-1}$[54]. The scientists also discovered that peanut husks can remove heavy metals effectively, with maximum adsorption ability of 7.7, 10.2, and 29.1 mg g-1 for Cr(III), Cu(II), and Pb(II), respectively [55].

Heavy metals were also removed from aqueous solutions using corncob. Researchers discovered a 25.00 highest adsorption capability with 5.10 mg g-1, as well as when the corncob was chemically modified, removal increased by 4-10-fold. with nitric and citric

acid[56]. Furthermore, records high adsorption efficiency of 16.20 $mg.g^{-1}$, corncob successfully removed Pb(II), When corncob was treated with sodium hydroxide, the extraction of Pb(II) with an enhanced adsorption efficiency 43.4 mg $g^{-1}$ [57].

Heavy metals have been removed from water sources using other types of vegetable waste. Heavy metals were successfully removed using mushroom residues which contains cellulose. Based on an analysis of four distinct kinds of mushroom residues, clearance efficiencies for Cu(II), Zn(II), and Hg(II) ranged from 39.70% to 81.70%[58]. Another study used three different mushrooms to remove Cd(II) and Pb(II), reached high adsorption ability of 35.00 and 33.80 $mg.g^{-1}$ respectively [59].

### 1.12 Scope of This Study

The primary goal of this study is to convert olive industry solid waste (OISW) which contains cellulose, hemicellulose, and lignin into value added polymer suitable for removing toxic metals from industrial wastewater, which have a strong affinity for metal ions adsorption and use them to remove harmful metals and organic particles from industrial waste water.

The specific objectives of this thesis are to:

1. Pretreated OISW from undesirable olive oil and other pollutants using several methods like Soxhlet extraction, until only the important ingredients (cellulose, hemicellulose, and lignin) left.
2. Synthesis new, derivatized OISW by adding carboxyl target functionality to OISW components, using CMC reaction.
3. Polymer treated thermally, in order to form a new chemical bond between OISW components.
4. Confirm the presence of the functional group at both derivatized OISW (Carboxymethylated OISW) and thermally treated derivatized Carboxymethylated OISW by FT-IR. And Study the thermal stability of the derivatized OISW using TGA instrument.
5. Determine the carboxyl content and the degree of substitution in the Derivatized OISW by back titration method. And determine the solubility of the new polymer.

And examine the viability of using the derivatized OISW in sewage water treatment from heavy metals specially Lead and Copper.

6. Determine the optimum adsorption efficiency for the polymer by studying the effect of various items including, solution pH, solution temperature, metal ion concentration and mixing time on temperature and using the optimum adsorption condition for the polymer into a real industrial waste water, to study the efficiency of our polymer to adsorb several heavy metals.

# Chapter Two
# Experimental Part

## 2.1 Basic Experimental

### 2.1.1 Chemicals and materials

Substance and all reagents used in this research (hydrochloric acid, ethyl acetate, sodium chloroacetate, acetic acid, methanol, sodium hydroxide, phenolphthalein, lead nitrate, copper (II) chloride dihydrate) were obtained from Sigma-Aldrich chemical company (Jerusalem) and utilized without any additional purification. Each reagent used was analytical grade, and the OISW (OLIVE INDUSTRY SOLID WASTE) used in this work was collected from an olive press in Talloza village/Nablus, Palestine**.**

### 2.1.2 Instruments and Methods

In this work, many instruments were used include pH meter (model: 3510, JENWAY), balance (Ohaus crop, item No AR 3130), water bath shaker (Daihan Lab tech, 20.00 to 250.00 rpm Digital Speed Control), Mass Spectrometer ICP-MS (ELAN 9000, ICE 3xxx C113500021 v1.30) used to measure the concentration of some heavy metals before and after react with our polymer. Nicolet 6700.00 Fourier transform infrared FT-IR Spectrometer (Waltham, MA, USA, Thermo Fisher Scientific) fitted by using Sensible Split Peaks Hemi Micro ATR device was used in order to recorded and check the chemical bonds of the synthesize polymer. The smart Split Peak is a micro sampling device for reducing the total reflectance. The device is adorned with a diamond ATR crystal. The following parameters have been used:4$cm^{-1}$ resolution, 400-4000 $cm^{-1}$ spectral range, 16 scans. Inductively Coupled Plasma (ICP), Thermo gravimetric analyzer (TGA) (Lenovo V520, China) as well as differential scanning calorimetry (DSC) instrument were carried out using a TG/DSC Star System (Mettler-Toledo) coupled with an MS-Thermostat GSD320 (Pfeiffer Vacuum) Mass Spectrometer, TG/DSC curves were measured with Pt crucibles in nitrogen gas flow (20 mLmin1) with a heating rate of 5 ºC $min^{-1}$ in the range 25-1100 ºC. The process was managed by the STAR software v.10.00 (Mettler Toledo). TGA was used to measure thermal stability, kinetic parameters for chemical reactions in polymers and alterations through chemical compositions.

Flame Atomic Absorption Spectrometer (FAAS) (Thermo Scientific, ICE 3000 series AA System). It was used to determine the concentration of residual metal ions in the studied solutions at 217 nm (FAAS used air-$C_2H_{2)}$. Analyses were carried out in triplicate (three samples run) and the average was reported, and the experimental data error was analyzed using Excel Microsoft software**.**

Atomic force microscope (AFM) instrument from pharmacy department used to determine the Nano scale image for the polymer surface, and the surface topography. Images were obtained in air at room temperature by depositing the sample on mica using a tapping mode-AFM (core AFM from Nanosurf company, Dyn190Al cantilever) was used with nominal spring constants of 48 N/m. Gwyddion software was used to analyze the images.

### 2.2 Derivatization of OISW Components

#### 2.2.1 Purification of (OISW) Using Acid Washes Technique

A 100.00 g of sample of dried OISW was grind by passing tit through a wily mill fitted with a 200-micron screen (Thomas Wiley® Mini Cutting Mills, Swedesboro, NJ 08085 USA). The sample was cleaned up from pollutants, dust, sand, soil. The grinded OISW was stirred with the acidic solution 0.50 L HCl at pH = 3.00 for 15.00min, filtered by suction filtration, then washed with distilled water. The OIWS were suspended in distilled water for 15.00 min, then filtered, and left to dry at room temperature.

#### 2.2.2 Soxhlet Extraction

Soxhlet extraction (Figure 2.1) is one of the most popular techniques for extraction of impurities from a solid material [60]**.** It was used to extract all the oil and residues remained in Jeft. The washed OISW about 100.00 g was placed in the extractor, a 500.00 ml of ethyl acetate was placed in a round bottom flask 1.00 L. The system was heated gently; ethyl acetate was evaporated and condensed above OISW until it covered completely. The ethyl acetate passed through the column dissolved oil and return back to the round flask bottom. Refluxing was continued in the next two and a half hours. The OISW sample was dried at room temperature and used in the following reactions.

**Figure 2.1**

*Soxhlet Extraction*

### 2.2.3 Making CMC from OISW (Carboxymethylation reaction)

A 10.00 g sample of purified OISW was placed in a three neck round bottom flask with a large magnetic bar. The flask fitted with a thermometer, a condenser attached to a nitrogen gas closed with a septum from the top fitted with inlet and outlet of nitrogen gas and the third neck was closed by a septum. 150.00 ml isopropyl alcohol and 15.00 ml distilled water were added to OISW while stirring. To the mixture, a 12.00 ml of 50.00% NaOH solution was added dropwise over 10.00 minutes with a syringe fitted through the septum. Then another 50.00 ml of isopropyl alcohol were added. After that sodium chloroacetate 21.00 g was added in one portion. The flask contents were heated to 62 °C in 30.00 min hour and kept at this temperature for 70 min.

At the end of the reaction period 8.00 ml acetic acid was added to neutralize the residual NaOH. Suction filtration was used to collect the produced precipitate of carboxymethylated OISW.

Which were then washed three times with a methanol and water solution 100.00 ml methanol and 40.00 ml water. Finally, it was washed with 50.00 ml methanol and dried

at room temperature. The mass of the produced carboxymethylated OISW polymer was 17.00 g Figure 2.2.

**Figure 2.2**

*Carboxymethylated OISW*

## 2.3 Thermal Curing

Thermal treatment is a remedial technique where solid materials such as polymers, sediments, soil or sludge, are heated to increase the mobility and facilitate the extraction of organic contaminants and heavy metals**.** Allow cross linking to happened and converting the functional group to chemical bonded composite[61]. Carboxymethylated OISW polymer was thermally treated at 160 ºC for 20.00 minutes.

## 2.4 Carboxyl Content of Carboxymethylated OISW

Back titration method was used to determine the carboxyl content in the derivatized OISW polymer [62].

### 2.4.1 Washing the Polymer

A 1.00 g sample of carboxymethylated OISW oven dried weight was stirred in a 100.00 ml of 0.50 M HCl solution at room temperature for 2.00 hours. Then it was rinsed many times with distilled water and soaked for 1.00 hour in distilled water until the HCl totally removed. The carboxymethylated OISW sample was collected by filtration.

### 2.4.2 Titration with HCl Solution

1.00 g of the acidified sample of carboxymethylated OISW was placed in a solution of NaOH (25.00 ml NaOH, 0.50 N) in a flask and stirred for 4 hours. The flask was sealed to prevents

The atmospheric carbon dioxide ($CO_2$) neutralization. After 4.00 hours, the solution was titrated with HCl 0.05 N solution in presence of 5.00 drops of phenolphthalein indicator. The end point reached after the addition of 17.20 ml HCl**.**

### 2.4.3 Determine blank volume

A blank was measured by titration of 25.00 ml 0.05 N Sodium hydroxide with 0.05 N Hydrochloric Acid using phenolphthalein indicator, in three trials, 24.36 ml of HCL was needed to reach the end point.

### 2.5 Water solubility of carboxymethylated OISW

A 1.00 g carboxymethylated OISW polymer was drenched in 25.00 ml water and stirred for 2 hours, collected by simple filtration, dried in oven adjusted at 60 °C for two hours. The polymer mass was weighed at room temperature, and 0.04 g reduction was recorded, that means the polymer solubility is 1.60% which is water insoluble.

### 2.6 Purification of Water Contaminated with Lead and Copper Metals using carboxymethylated OISW

#### 2.6.1 Lead(II) Solutions Preparation

A 1.5985 g of lead nitrate $Pb(NO_3)_2$ were dissolved in distilled water, and then the solution was diluted to a 1.00 L volumetric flask to produce a stock solution with a 1000 ppm concentration. From this solution 5.00 standard solutions with the concentrations of 5.00, 10.00, 20.00, and 50.00 ppm of lead $Pb^{2+}$ were prepared.

#### 2.6.2 Preparation of copper (II) Solution

A stock solution with a concentration of a 1000 ppm of Copper ion Cu(II) was prepared by dissolving 2.683 g of copper chloride dihydrate $CuCl_2.2H_2O$ in distilled water and then diluting to 1000 mL in a volumetric flask. From this solution 5 standard solutions

with concentrations of 5.00, 10.00, 20.00, and 50.00 ppm of copper Cu(II) were prepared.

### 2.6.3 Calibration Curves

The calibration curves for the standard solutions were formed by measuring the absorbance of the standard solutions for copper(II) and lead(II) ions, it was plotted using flame atomic adsorption spectroscopy (FAAS). Figures 2.3 and 2.4 show the calibration curves for $Pb^{2+}$ and as well as $Cu^{2+}$ ions, respectively.

**Figure 2.3**

*Lead Pb(II) Calibration Curve*

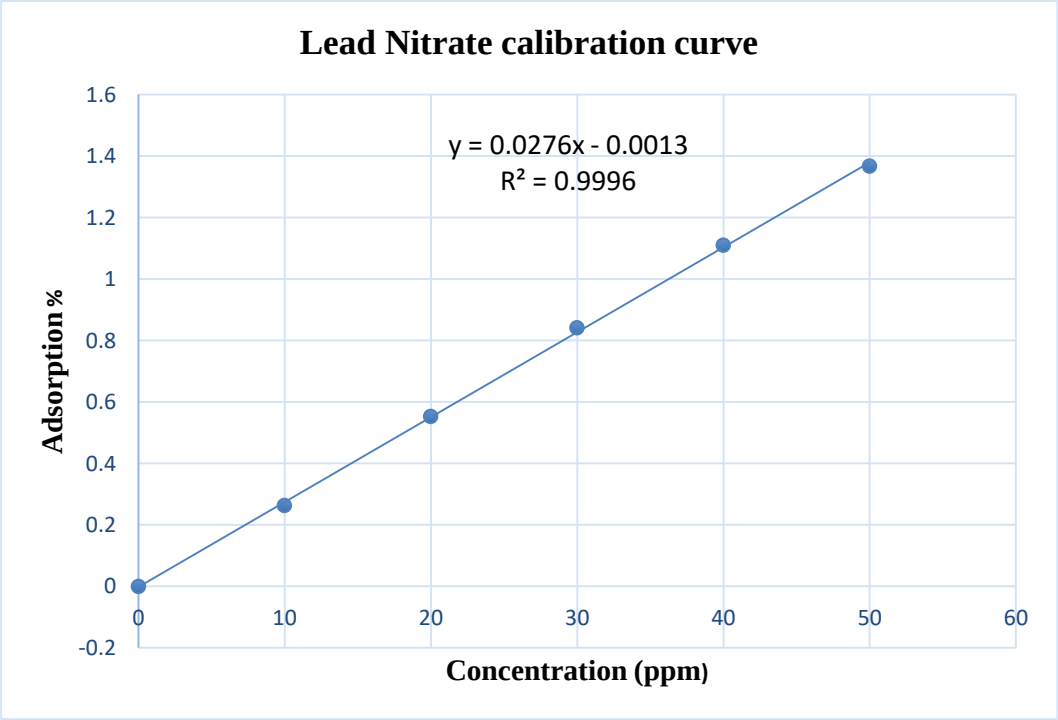
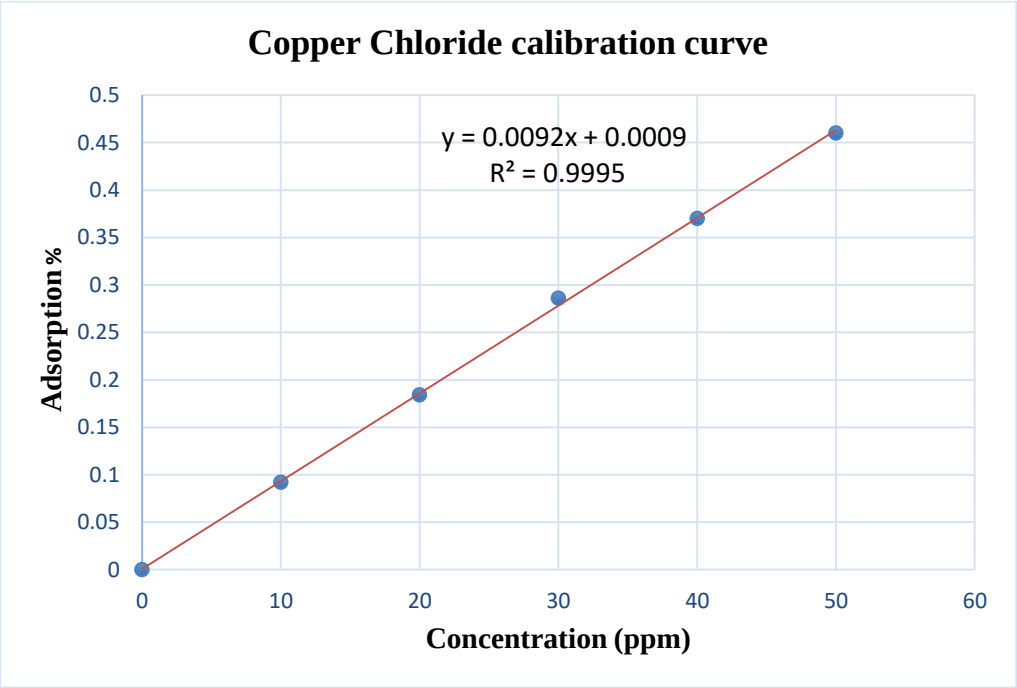


**Figure 2.4**

*Copper Cu(II) Calibration curve*




To evaluate the impact of several factors, including initial concentration, time, dosage, pH, and temperature at the effectiveness of hazardous metal removal by carboxymethylated OISW polymer, calibration curves for both ions were plotted using the generated standard solutions. All of the tested solutions' adsorption was quantified using FAAS (Flame Atomic Absorption) at a wavelength of 217.00 nm for lead(II) and 324.8 nm for copper(II). Using the resulting curves, the concentrations of residual lead ions in the filtered samples were estimated using the calibration curve for Pb(II) ions to measure, the standard solutions' absorbance, as well as copper(II) ions two. Figures 2.3 and 2.4, display the calibration curves for Cu(II) and Pb(II), ions respectively.

**Extraction by Batch Adsorption process**

The extraction was done in stages, whereas specified quantity of carboxymethylated OISW polymer was added to lead(II) solution or copper(II) solutions in a vial with a specified concentration, then the vial was sealed and shacked at constant temperature and constant pH mechanically at a rate of 125.00 period/min, based on the factor under tested, for a specific period of time. Using a syringe, a sample of each mixture was collected. A 0.45 m syringe filter was used to filter the solution, and then analyzed for

residual metal ion concentrations. The concentration of lead and copper metals were determined by atomic absorption spectroscopy AAS.

### 2.6.4 Carboxymethylated OISW dose effect on removal efficiency of Pb(II) and Cu(II)

To figure out the optimal amount of carboxymethylated OISW for Copper(II) and Pb(II) adsorption, different quantities of the carboxymethylated OISW (10.00 mg, 20.00 mg, 30.00mg, 40.00 mg, 50.00 mg) were added to five plastic bottles containing 10.00 mL with 20.00 ppm metal ion standard solution. The pH of the solution was adjusted to 4.50 and were shaken at 25 ºC for 30.00 minutes using thermostat shaker. FAAS was used to determine the concentrations of metal ions in the filtrate at 20 ºC. Table 2.1 displays the results of the Carboxymethylated OISW dosage effect on the adsorption of both copper(II) and lead(II) ions.

**Table 2.1**

*Carboxymethylated OISW dose effect on removal efficiency of Pb(II) and Cu(II)*

| Polymer dose (mg) | $[Pb]^{2+}$ (ppm) | Removal of Pb(II) (% ) | $[Cu]^{2+}$ (ppm) | Removal of Cu(II) (% ) |
|---|---|---|---|---|
| 10 | 9.3214 | 53% | 9.6412 | 51% |
| 20 | 7.5322 | 62% | 8.6398 | 56% |
| 30 | 5.0412 | 74% | 7.4322 | 62% |
| 40 | 7.1271 | 72% | 5.9112 | 70% |
| 50 | 8.4837 | 70% | 4.7891 | 76% |

### 2.6.5 Adsorbate Concentration Effect

To determine the optimal concentration of copper(II) and lead(II) ions solutions, the perfect dosage of Carboxymethylated OISW polymer 50.00 mg for copper and 30.00 mg for lead was added to five plastic bottles, possessing 10.00 mL of various standard Copper(II) and lead(II) concentrations (1.00 ppm, 5.00 ppm, 10.00 ppm, 20.00 ppm, and 50.00 ppm) was shaken mechanically under these conditions pH 4.50, 30.00 min contact time and temperature 25 ºC.

Table 2.2. shows concentration of metal ions in each filtrate using FAAS.

**Table 2.2**

*The effect of an adsorbent concentration*

| Concentration (ppm) | $[Pb]^{2+}$ ppm | Removal of Pb(II) (% ) | $[Cu]^{2+}$ Ppm | Removal of Cu(II) (%) |
|---|---|---|---|---|
| 1 | 0.8840 | 11% | 0.754 | 24.6% |
| 5 | 3.9643 | 20 % | 2.27 | 54.6% |
| 10 | 6.9800 | 30% | 2.648 | 73.5% |
| 20 | 5.0521 | 74% | 4.7705 | 76% |
| 50 | 10.5816 | 78% | 9.2315 | 81% |

### 2.6.6 Contact Time Effect

Metal ion adsorption on every adsorbent were investigated as a function of contact time at the optimized Carboxymethylated OISW dose and optimized adsorbate concentration.

Five solutions of both lead nitrate and copper chloride with optimum concentration (50.0 ppm) were placed in five vials, then the Carboxymethylated OISW dosage that gave maximum removal efficiency 50.00 mg polymer with copper ion, 30.00 mg polymer with lead ion was added to each solution, then shacked mechanically at 4.5 pH and 25 ºC for various times (1.00 , 10.00 , 20.00 , 30.00, and 60.00 ) minutes, and at the end of each period , the metal ion concentration of both $Cu^{2+}$ & $Pb^{2+}$ in each filtrate was measured using FAAS and summarized in table 2.3.

**Table 2.3**

*contact time Effect on the adsorption of copper(II) and Lead(II) on the carboxymethylated OISW*

| Contact time (min) | $[Pb^{2+}]$ (ppm) | Removal of Pb(II) (% ) | $[Cu^{2+}]$ (ppm) | Removal of Cu(II) (%) |
|---|---|---|---|---|
| 1 | 16.9125 | 66% | 15.2523 | 69% |
| 10 | 15.4064 | 69% | 13.6583 | 72% |
| 20 | 14.9600 | 70% | 10.7825 | 78% |
| 30 | 10.7870 | 78% | 9.1745 | 81% |
| 60 | 10.2781 | 79% | 3.5976 | 92% |

### 2.6.7 Effect of Temperature

In order to examine how temperature affects the adsorption process, 10.00 mL of $Cu^{+2}$ with a 50.00 ppm standard solution and 50.00 mg of the carboxymethylated OISW polymer were combined, also 30.00 mg derivatized OISW polymer added to 10.00 mL of $Pb^{2+}$ , 50.00 ppm standard solution at pH of 4.50. Each solution was shaken mechanically in water bath at the varying temperature (15, 20, 30, 40 and 60 ºC) to the optimum time 60.00 min. At the end of each time interval, metal ion concentration of both $Cu^{+2}$ & $Pb^{+2}$ in each filtrate was measured using FAAS and summarized in Table 2.4.

**Table 2.4**

*Temperature Effect on the adsorption for $Cu^{2+}$ & $Pb^{2+}$ ions on Carboxymethylated OISW*

| Temp $^oC$ | $[Pb]^{2+}$ (ppm) | Removal of Pb(II) (% ) | $[Cu]^{2+}$ (ppm) | Removal of Cu(II) (%) |
|---|---|---|---|---|
| 15 | 16.7322 | 66% | 13.0532 | 73% |
| 20 | 9.1681 | 81% | 2.3210 | 95% |
| 30 | 10.9456 | 78% | 5.0120 | 89% |
| 40 | 17.5542 | 64% | 8.9790 | 82% |
| 60 | 28.4532 | 43% | 17.0843 | 65% |

### 2.6.8 pH Effect

Adsorption was investigated in numerous solutions ranging from acidic pH = 3.00 to basic mediums pH =11.50 so as to study pH influence on the adsorption process. Using solutions of 0.10 M HCl and 0.10 M NaOH, the pH values were adjusted. The optimum conditions of contact time 60.00 minutes, adsorbate concentration 50.00ppm, at temperature of 20.0ºC for both, and Carboxymethylated OISW polymer dosage 30.00 mg for $Pb^{2+}$ and 50.00 mg for $Cu^{2+}$ were used for each pH value. A 10.00 ml solution of each was shaken mechanically in water bath at the desired pH value (3, 4.5, 6, 7, 9, and 11.5). FAAS was used to measure the metal ion concentration for both $Cu^{2+}$ and $Pb^{2+}$ in each filtrate, and the values are shown in table 2.5.

**Table 2.5**

*pH value Effect on the adsorption of $Cu^{+2}$ & $Pb^{+2}$ ions on the Carboxymethylated OISW*

| PH | $[Pb]^{2+}$ (ppm) | Removal of Pb(II) (% ) | $[Cu]^{2+}$ (ppm) | Removal of Cu(II) (%) |
|---|---|---|---|---|
| 3 | 9.0639 | 81% | 12.0167 | 75% |
| 4.5 | 8.4438 | 83% | 6.9140 | 86% |
| 6 | 7.1219 | 85% | 3.2657 | 93% |
| 7 | 9.5346 | 80% | 10.7963 | 78% |
| 9 | 11.8732 | 76% | 14.6512 | 70% |
| 11.5 | 13.6793 | 72% | 20.4467 | 59% |

## 2.7 Adsorption Isotherm

This method was used to determine the type of mechanism the adsorption proceed. Adsorption can be described using two models Langmuir isotherm model which describes monolayer coverage of adsorption surface, and Freundlich isotherm model which describes multilayer adsorption, these two models will be discussed in details in chapter three of this work.

## 2.8 Adsorption Kinetic

To realize the mechanism of the metal ions adsorption process by the carboxymethylated OISW polymer, the results were applied to the kinetic laws. The ideal pH, contact time, temperature, polymer dosage, and metal ion concentration were used to study the adsorption kinetics. We measured the metal ion concentration both before and after adsorption. The experimental part was performed using 30.00 mg of the carboxymethylated OISW were insert to 10.00 mL of a 50.00 ppm of Pb(II) solutions at pH 6.00 and shaken for 60.00 minutes at 20ºC. And 50.00mg of carboxymethylated OISW polymer with 50.00 ppm Cu(II) solution was also studied under the optimized conditions. Measurements of the adsorption rate and comparisons to theoretical models were made. At varied contact times, the experimental results were used to the pseudo-kinetic concepts of the first and second orders. On the Carboxymethylated OISW polymer, parameters of the pseudo first and pseudo second order kinetic models (K, qe,

and $R_2$) of ions adsorption were determined. The estimated and observed qe values were examined [63].

### 2.9 Adsorption Thermodynamic

To assess the appropriateness and spontaneity of such a process, it is required to investigate the thermodynamics of the adsorption process. By computing thermodynamic parameters like the change in entropy (ΔS), and change in free energy (ΔG), change in enthalpy(ΔH), the behavior of the adsorption process may be investigated. The following equation represents a summary of the relationship between the adsorption parameters[63].

$$\Delta G = \Delta H - T\Delta S \qquad \text{Eq. 1}$$

In which; ΔS is the change in entropy (J/K), ΔH is the change in enthalpy (J), and ΔG is the change in Gibbs free energy (J). ΔG is referred to the thermodynamic equilibrium constant (Kd) using the given formula: ΔG = -RT InKd (Eq. 2) in which, T: the absolute temperature (K) and Kd: the thermodynamic equilibrium constant that equals (qe/Ce) with a unit of mol or (L/g). R: the universal gas constant that equals 8.314 $J.mol^{-1}$. $K^{-1}$, Substituting equation 2 into equation1.

and reordering results in:

$$\ln Kd = \Delta S\, R - \Delta H\, R \qquad \text{Eq. 2}$$

A Van't Hoff plot of $InK_d$ versus (1 /T) generates a straight line with a slope of (- ΔH/ *R*) and a y-intercept equal to (ΔS /R).

## 2.10 Purification of real Wastewater sample

This study used a sample of sewage water collected from a paint factory in (Jericho/Palestine). The sample was subject to analysis by ICP-AES (the analysis was performed by the Water Center at An-Najah National University, Nablus, Palestine) to determine the metals content and their concentrations. Three vials were each loaded with a 10 ml of the wastewater. One of them of vials was used as a blank a, to the second vial a 50.00 mg of derivatized OISW polymer was added and 30.00 mg to the third vial. The adsorption was performed under the determined optimum conditions pH = 6 and 60 min mechanically shaking at 20 ºC. The results of the ICP-AES analysis for residual metal ions concentrations are provided in table 3.6-page 44.A quantity of each combination was taken out using a syringe and filtered through a 0.45 m syringe filter.

# Chapter Three
# Results and Disscusion

## 3.1 Derivatization of OISW component

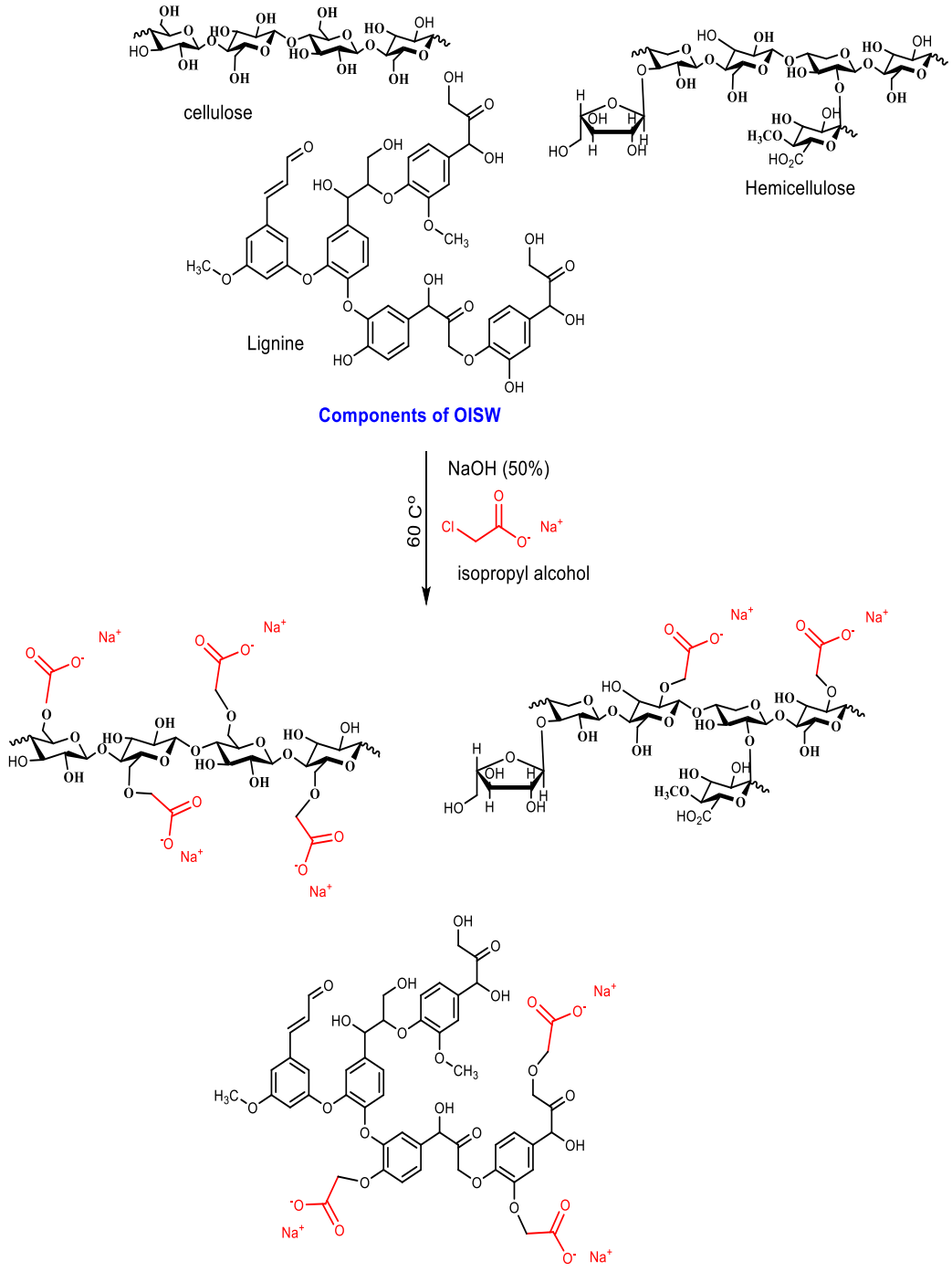
The current study involved converting olive industry solid waste to value added material. It was functionalized with ionic functionality (carboxyl groups). It was designed, synthesized, developed, thermal bonded, characterized, and used in wastewater purification as a metal adsorbent for heavy metals specifically Lead and Copper ions. The importance of this work is that the raw material olive industry solid waste used for this purpose. It has many attractive features natural byproduct, commercially available, cheap and environmentally friendly. Also, the OISW distinguished by having cellulose, hemicelluloses and lignin as part of its composition, and the three components carry hydroxyl groups in their building blocks. The main purpose of this work is to convert OISW into a valuable-added material. OISW with ionic functionality was prepared by reacting with sodium chloroacetate in alkali medium and isopropyl alcohol as a solvent. And since it is rich in hydroxyl groups, so that in alkali medium it behaves as nucleophile and undergoes nucleophilic substitution

reaction with a material that contains a leaving group such as sodium chloroacetate. The addition of carboxymethyl group to cellulose, lignin and hemicelluloses make them has high affinity for metal ions. The presence of carboxyl, as well as hydroxyl group, and the aromatic ring on OISW components makes it excellent candidate for wastewater purification, since carboxyl and aryl groups considered as excellent chelating agent for metals.

The first step of derivatization includes purification of the OISW from residual olive oil and other hydrophobic components [64]. This was done by subjecting the OISW to Soxhlet extraction using polar solvent water and the non-polar solvent ethyl acetate in two different steps. This technique would improve the efficiency of alkalization and carboxymethylation at the next step in additions it reduces the extractives [65].

**Scheme 3.1**

*The chemical reaction of adding ionic functionality to OISW components.*

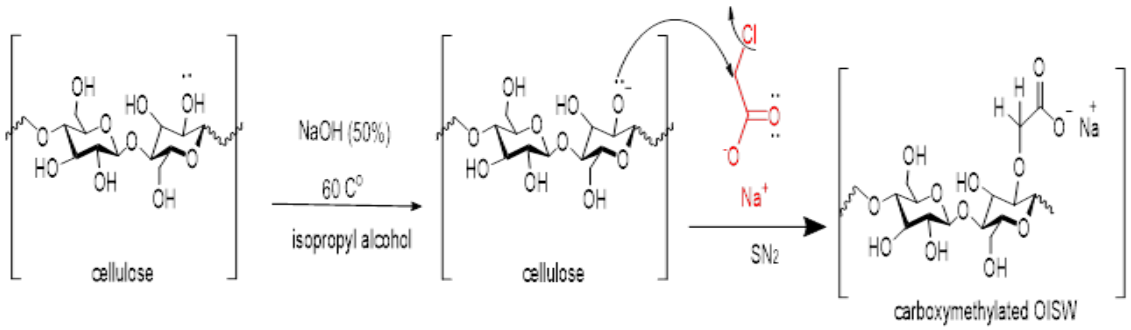



Then the purified OISW was derivatized as a mixture by three step processes that include treatment with a 50.00% NaOH solution in order to deprotonate the hydroxyl group and convert it to a strong nucleophile [62]. The second step involved carboxymethylation which was accomplished by reacting it sodium chloroacetate[66]. in presence of isopropyl alcohol as shown (Schemes 3.1). A detailed mechanism of the

reaction is shown in scheme 3.2. Acetic acid, methanol and distilled water were used in product washing and neutralization[67].

**Scheme 3.2**

*Reaction mechanism of cellulose carboxymethylation*




### 3.2 Carboxyl Content of the Carboxymethylated OISW

In the carboxymethylation process of the OISW carboxyl group was added to the OISW, since the carboxyl content has an important impact on its polarity, thermal and mechanical properties. The efficiency to adsorb toxic metal will increase[68], for that reason it is very important to determine quantitatively the carboxyl content by using the back-titration method as mentioned in experimental part sec. 2.4. The derivatized OISW was soaked with sodium hydroxide and titrated with known concentration of HCl solution in presence of phenolphthalein as an indicator. The carboxyl content of derivatized OISW was calculated using equation 1.3:

Carboxymethyl content (mmol/100 grams)

$$= 100*(V_{blank}-V_{sample})_{HCL} * (N_{HCL}/0.25) \qquad \text{Eq 1.3.}$$

From Eq1.3 and the reaction conditions mentioned in sec.2.4, the calculated carboxyl methyl content was 143.2 mmoles/100 grams.

### 3.3 Calculated the degree of substitution

The degree of substitution (DS) can be defined as: the average number of substituent groups attached per base unit. The (DS) affects markedly the properties of Carboxymethylated OISW [69].

The DS was calculated to be 0.310 Degree using equation 2.3.

DS = CM Content mmol/100grams*162 g/mole/(1000mmol/mol) *100 g). Eq 2.3

### 3.4 Characterization by FT-IR

As seen in figure 3.1. A, many peaks appeared for OISW, at 2924 $cm^{-1}$ corresponding to C-H stretching, peak at 1048 $cm^{-1}$ might be related to the C-O bending peak that confirms the presence of carbohydrates in the OISW. From figure 3.1. B, no obvious change in the frequency occurred after washing the OISW, and this is an evidence for OISW insolubility and stability. From the IR spectra for Carboxymethylated OISW fig. 3.1.C, It presents a new sharp peak at 1594 $cm^{-1}$ that is reasonable for the carbonyl group of the carboxylate. Another peak at 1052 $cm^{-1}$ refers to glycosidic linkage in the carbohydrate components[70]. The peak observed at 1325 $cm^{-1}$ it can be rationalized for new stretching alkyl group formed in the derivatization. Finally, there is a clear peak at 3404 $cm^{-1}$, which is a clue for O-H starching hydroxyl group of carboxylic acid, and its bending peak at 1415 $cm^{-1}$, and this peak was disappear after thermal treatment (figure 3.1.D) that means heating up converted the carboxyl OH into carboxylate ion. Also, from (fig 3.1.D) the derivatized OISW after cross linking, it was clear that the thermal treatment enhanced the Carboxymethylated OISW. A narrow weak peak at 1748 was noticed, we believe that it is for anew carbonyl group produced by cross linking (easter linkage) this an evidence that thermal curing was successfully accomplished.

**Figure 3.1.A**

*FT-IR of olive industry solid waste*

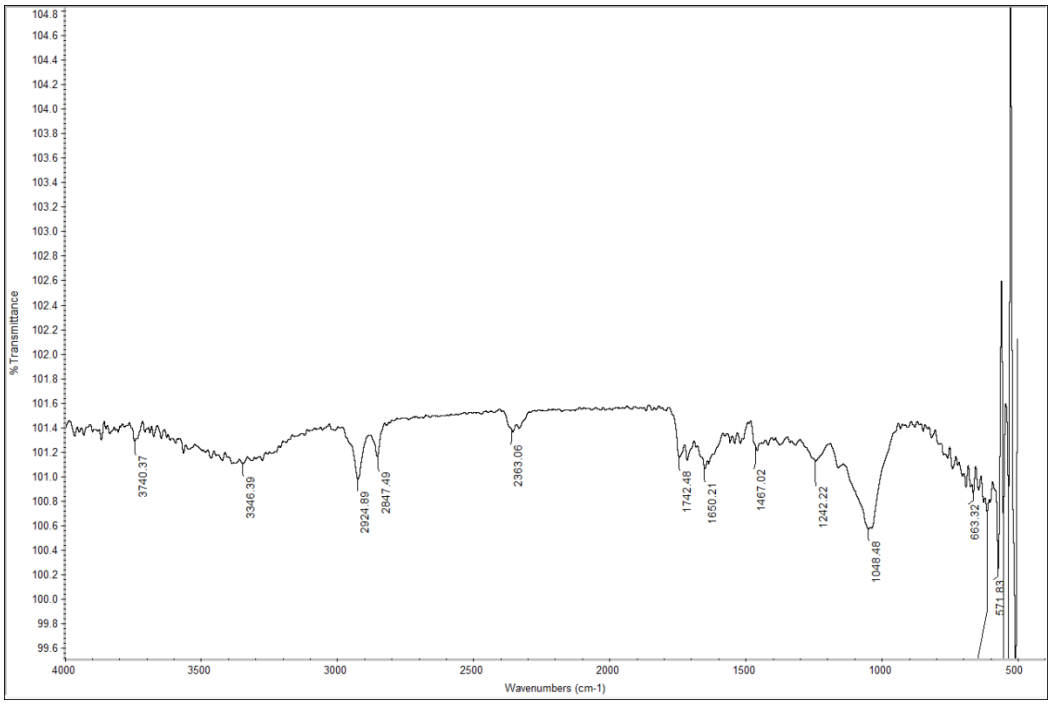



**Figure 3.1.B**

*FT-IR of olive industry solid waste after Thermal treatment*

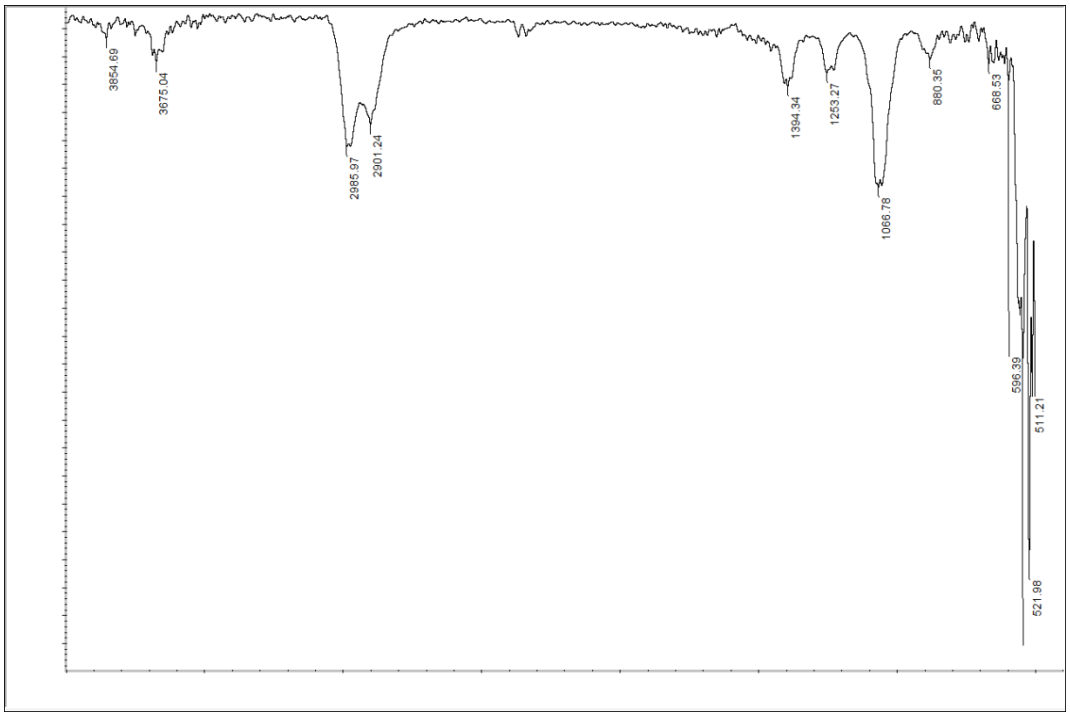


**Figure 3.1.C**

*FT-IR of Carboxymethylated OISW*

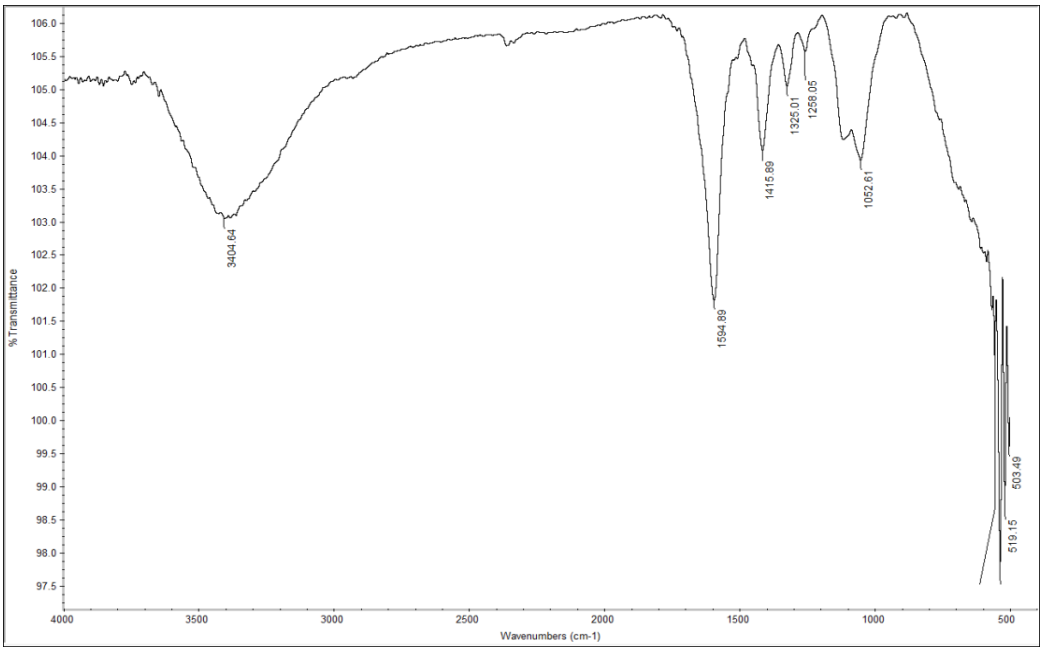
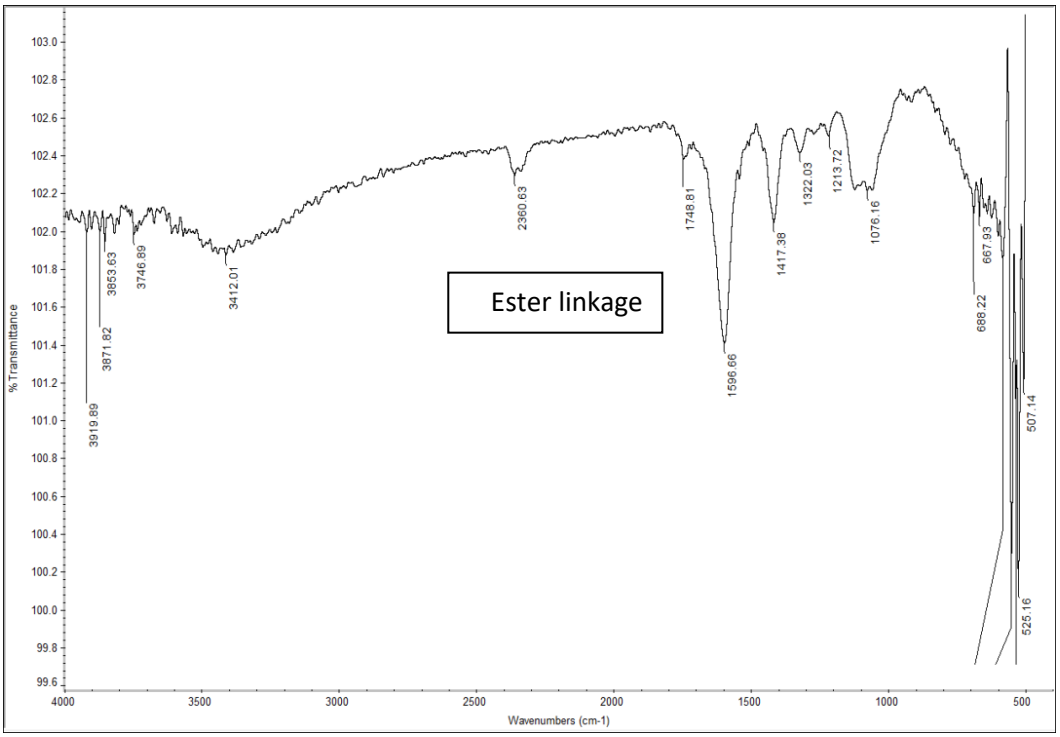



**Figure 3.1.D**

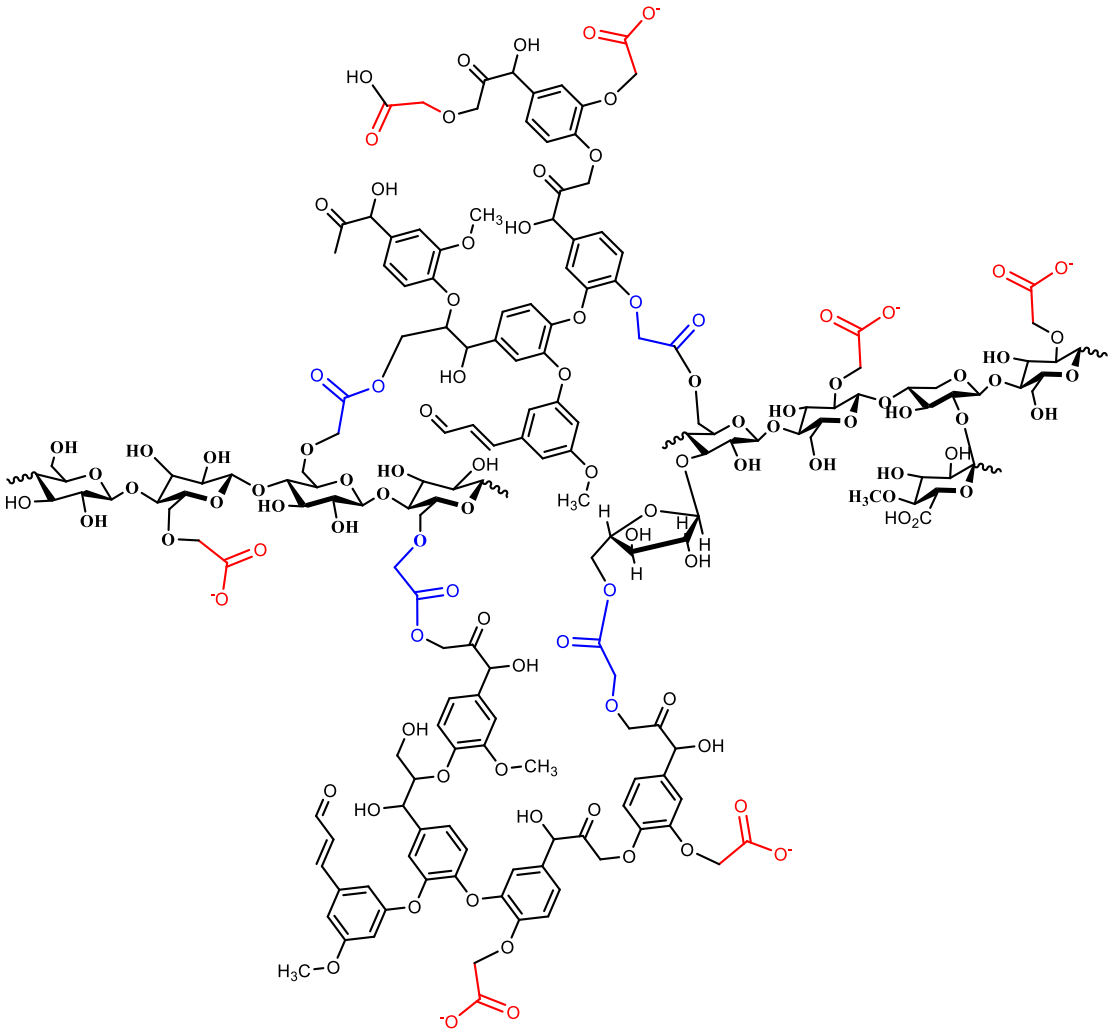
*Derivatized OISW after thermal curing*



The thermal treatment causes the three components of the OISW cellulose, hemicellulose, and lignin to bond covalently (crosslink) via ester linkage to form a net of 3D highly stable structure and loaded with chelating functional groups for toxic metals as shown in scheme 3.3.

**Scheme 3.3**

*A representative 3D structure forms from thermal curing of carboxymethylated OISW*



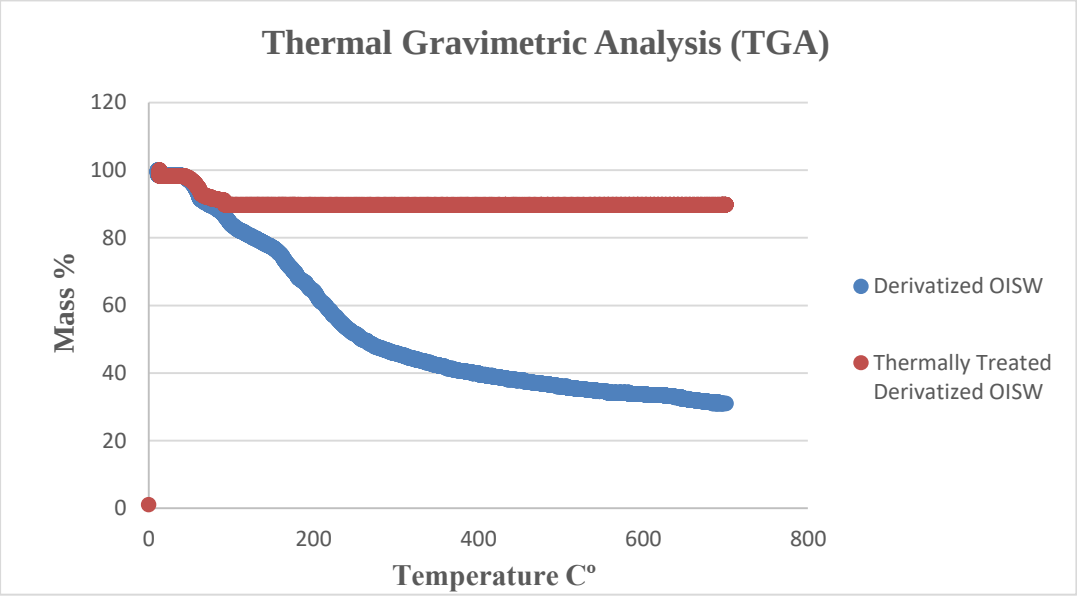
### 3.5 Characterization by Thermal Gravimetric Analysis TGA

Thermal stability was measured via TGA analysis, which involved measuring the mass of every sample through time as a temperature function and declaring the polymer thermal stability at high temperatures. Two samples of Carboxymethylated OISW were subjected to TGA, one was thermally heated and the second not heated. The results are shown in figure 3.3, the graph shows the mass lost for each polymer as temperature rises. Both polymers are relatively stable from the graph results. For the carboxymethylated OISW as the temperature increases, the mass decreases, and at 700 $^{o}$C, 30% of the sample remained, which is a remarkable result.

On the other hand at 700 $^{o}$C , 89.00% of the sample remained for the thermally treatment carboxymethylated OISW and it was remarkable too. This means the polymers are high thermally stable and had a very organized crystals, and this result also support our theory that thermally treated (curing) derivatized OISW had a 3D structure.

**Figure 3.2**

*Thermal Gravimetric Analysis for Carboxymethylated OISW*



## 3.6 Characterization by AFM (Atomic Force Microscope)

Figures 3.3.A shows that the average diameter for the derivatized OISW, was 30 ± *2* nm, and figure 3.3.B shows that for thermally treated OISW, it was 300 ± 15 nm. A new cross-linking chemical bond had formed, so the size of pores and the polymer surface changed and improved. Its impressive how thermally treated OISW have a big surface area with a little pore. The surface has almost a cluster shape, which provides the adsorption process. For this reason, the thermally treated OISW were used in the followed parts [71].

**Figure 3.3.A**

*Atomic force microscope image for Carboxymethylated OISW*

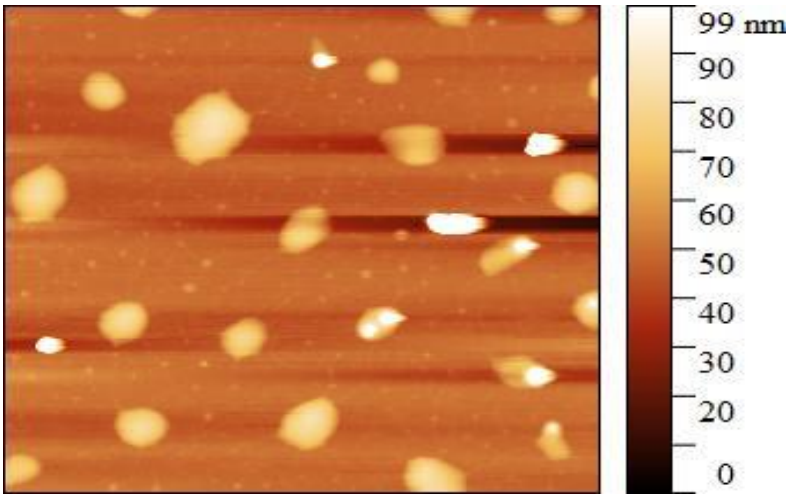
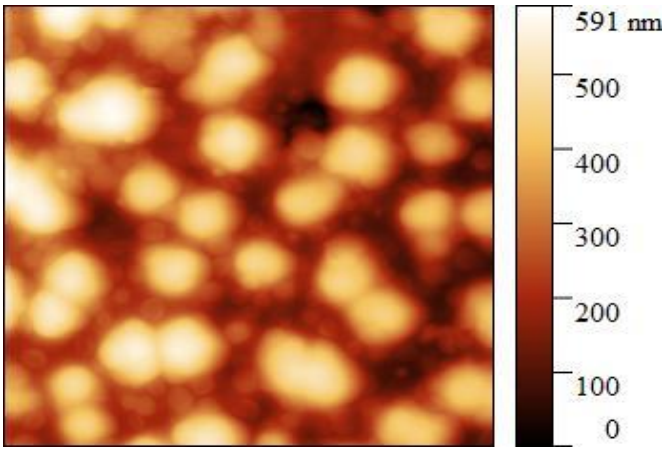



**Figure 3.3.B**

*Atomic force microscope image for thermally curing Carboxymethylated OISW*



### 3.7 Adsorption Results

In this work, the main objective is to use derivatized OISW for removing toxic, heavy metals from industrial wastewater. This operation was accomplished by studying ability of derivatized OISW toward the adsorption of lead(II) and copper(II) ions. As mentioned at sec. 2.6. The remained concentrations of heavy metal ions were analyzed using Flame Atomic Absorption Spectrometer, and the percentage of removal was calculated using equation 3.3.

$$\% \text{ adsorption} = (Ci - Cf / Ci) \times 100\% \qquad \text{Eq. 3.3}$$

In which: $C_i$ = heavy metal ion's initial concentration in the solution (ppm).

$C_f$ = Heavy metal ion final concentrations in solutions (ppm).

Under experimental conditions, the adsorption capacity qe (mg/g) was estimated for varied ion concentrations at equilibrium, equation 4.3 below shows that[45]:

$$q_e = (C_i - C_f / m) * V \qquad \text{Eq. 4.3}$$

In which; m is the mass of the adsorbent (g), and V is the volume of the solution (L).

#### 3.7.1 Carboxymethylated OISW dosage Effect on adsorption Pb(II) and Cu(II) ions

To determine the optimum amount of adsorbent Carboxymethylated OISW that gave the best and highest adsorption percentage, the solutions concentration, temperature, volume, pH, and the shaking time were set at, 20 ppm, 25 $C^o$ , 20 ml, 4.5, and 30 minutes, respectively. The highest removal was obtained at the addition of 50 mg of Carboxymethylated OISW adsorbent for $Cu^{2+}$ removing, and 30 mg Carboxymethylated OISW for $Pb^{2+}$ removal as (figure 3.4) at appendix B shows.

For lead ($Pb^{2+}$), as the polymer dosage increase, adsorption increase, till reached the highest adsorption percentage at 30.00 mg of derivatized OISW with a removal efficiency of 74%, when the dosage amount was low. The active sites at the surface were available and empty, and then after 30.00 mg as the polymer dosage increase, adsorption almost remain constant, because the active sites at the polymer were gradually occupied by lead ions. Thus 30.00 mg were chosen as the optimum dose for lead(II) solutions purification.

However, flame atomic adsorption spectroscopy (FAAS) results showed that the amount of $Cu^{2+}$ ions adsorbed were increased by increasing the polymer dose, as the amount of polymer increase, the adsorption increases. A 50.00 mg of carboxymethyl OISW was chosen as an optimum dose for $Cu^{2+}$ solution, because it gave the maximum adsorption percentage of about 76.00%.

### 3.7.2 Metal ion concentration effect on adsorption Pb(II) and Cu(II)

To investigate the influence of metal ion concentration on adsorption of $Pb^{2+}$, $Cu^{2+}$ metal ions onto Carboxymethylated OISW, the optimum amount of polymer was fixed at 50.0 mg, 30.0 mg for copper and lead solutions respectively. The other parameters, (temperature, PH, shaking time, solution volume) were adjusted at 25 $C^{o}$ , 4.5, 30 minutes, and 10.00ml as mentioned in experimental part sec. 2.6.5. The results showed in figure 3.5 at appendix B over a concentration range from 1-50 ppm.

As figure 3.5 at appendix B shows for both copper and lead, a proportional relationship was noticed between metal ion concentration and the adsorption. The adsorption increased with metals concentration up to 20ppm with 74%, 76%, for $Pb^{2+}$, $Cu^{2+}$ solutions respectively. after that slightly increment were observed, with 78% ,81%, for $Pb^{+2}$, $Cu^{+2}$ solutions respectively at 50.0 ppm. So that 50.0 ppm was selected as the optimized concentration for both lead and copper, and this means that the polymer is efficient for the high ion concentrations, and mild for lower concentration. These results indicate that, the adsorption percentage was increased with increasing concentration, since the carboxymethyl OISW has unlimited binding active sites on the surface, that can adsorb heavy metal according to scheme 3.3.

### 3.7.3 Contact time Effect

Under certain constant circumstances of pH 4.5, adsorption temperature 25 $^{o}$C, ideal ions concentration 50.00 ppm, volume of adsorbate 10.00 ml, and adsorbent dose 50.00, 30.00 mg for copper and lead respectively, adsorption of lead(II) and copper(II) metal ions by carboxymethylated OISW was investigated as a function of time. The contact time that tends to give the ideal contact time was chosen to have the lowest remaining metal ion concentration. From the results obtained from the procedure (sec 2.6.6) and using contact time values ranging from 0-60 minutes are presented in figure 3.6 at appendix B.

A direct proportional relationship was recognized between contact time and adsorption percentage. As the contact time increased, the adsorption was increased, which means that this polymer is a time dependent. And from the obtained data shows, as contact time increased and the abundance of vacant sites at the outer surface not only the polymer active site occupied, but also the interior pores started to be filled[63], so longer time required for reach the equilibrium with

solution. It was found that 60.00 min of contact is the optimum for both ions, $Pb^{2+}$, $Cu^{2+}$ with 79% removal for $Pb^{2+,}$ however after 30.00 min no serious change in adsorption percent (only 1%). On the other hand, regarding to $Cu^{2+}$, 92% removal was observed, and after 30 min the copper ion adsorption increased from 81% up to 92%, that means affected by increasing contact time. These phenomena may be related to the ion character mainly the size of $Cu^{2+}$ ion.

### 3.7.4 Temperature Effect

To investigate the temperature influence on Pb(II), Cu(II) adsorption by Carboxymethylated OISW, the optimum conditions for dosage, concentration, contact time, remained constant at 50.0 mg for $Cu^{2+}$ solution,30.0 mg for $Pb^{2+}$ solution, (50.00 ppm, 60.00 min) for both. Figure 3.7 at appendix B summarized the results ranging from (15 -60) C$^{o}$, as results collected from the procedure (sec. 2.6.7).

Figure 3.7 at appendix B shows that adsorption decreased as the temperature increased, maximum %removal was at 20 $^{o}$C , with removal of 81%, 95% for $Pb^{2+}$, $Cu^{2+}$, respectively, so it is considered to be the optimum temperature. The results indicate

that the adsorption prosses of Carboxymethylated OISW of $Pb^{2+}$, $Cu^{2+}$ ions occurred spontaneously and exothermic. The kinetic energy of the adsorbed particles on the adsorbent surface increases as the temperature rises and this increases the probability of their separation from the adsorbent surface [72, 73]. Also the decline in adsorption at higher temperature can be related to increase the solubility of ions with temperature [74].

### 3.7.5 Effect of pH on Adsorption Process

The pH of the solution is an important factor in controlling the adsorption process efficiency. Under the optimized experimental conditions (50.00 ppm solution concentration, 60.00 min, contact time, temperature 20 $^{o}$C, and Carboxymethylated OISW,50.00 mg, 30.00 mg for $Cu^{2+}$, $Pb^{2+}$ solutions, respectively), the effect of pH on adsorption performance of derivatized OISW was investigated as mentioned in experimental part (sec. 2.6.8). The results are represented in figure 3.8 at appendix B of pH value ranging from acidic, pH = 3.0 to basic mediums pH = 11.5.

Figure 3.8 at appendix B shows that the maximum adsorption for both ions occurred at a pH of 6.00. In case of lead ion, the change was not serious with increasing the pH value, and this situation of results was obtained for contact time parameter investigations. On the contrary for copper ion as pH value increased, adsorption increased up and reached the highest at pH = 6.00 then decreased which means prefers acidic medium over alkaline one. Adsorption rate seems to be constant when the surface is barely occupied at acidic medium until 6.00 pH value. Transfer to basic medium decrease the adsorption. After achieving the ideal pH for Carboxymethylated OISW, the $Pb^{2+}$ and $Cu^{2+}$ removal ratio started to decline, this can be attributed to the fact that, at higher pH metal oxide stats forming [75].

### 3.8 Optimum adsorption parameters

The optimum adsorption parameters for the two ions ($Cu^{2+}$, $Pb^{2+}$ ) are summarized in table 3.1.

**Table 3.1**

*Optimum Adsorption Parameters for lead, copper ions*

| Adsorbent | Metal ion | %Adsorption | Parameters Adsorbent dosage (mg), concentration (ppm), Contact time (min), Temp (°C), pH |
|---|---|---|---|
| **Carboxymethylated OISW** | $Pb^{2+}$ | 85% | 30, 50, 60, 20,6 |
| **Carboxymethylated OISW** | $Cu^{2+}$ | 93% | 50, 50, 60, 20, 6 |

### 3.9 Adsorption isotherm

To investigate the efficiency of the prepared polymers in removing both ions, $Cu^{2+}$ and $Pb^{2+}$ at equilibrium, the Langmuir (Eq. 6.3) and Freundlich (Eq. 8.3) isotherms were used. When the ions are grouped in a single layer on the surface of the polymer, Langmuir model guides adsorption process. The Freundlich model is utilized when several heterogeneous layers are used for the adsorption process between the ions and the polymer surface [76].

#### 3.9.1 Langmuir adsorption isotherm

The Langmuir adsorption isotherm describes monolayer coverage of adsorption surface, also defines the equilibrium between an adsorbate and an adsorbent system at which adsorbate adsorption is limited to one molecular layer, before or at a relative pressure of unity is reached. If the figure plot between 1/q vs1/c gives a straight line with high $R^2$ value so the adsorption obeys this model.

$$1/q_e = 1/ (Q_{max} K_l C_e) + 1/Q_{max} \qquad \text{Eq .6.3}$$

Where;

$C_e$: the ion equilibrium concentration (ppm).

At equilibrium, $q_e$ is the mass of adsorbate adsorbed per unit mass of polymer (mg/g).

$Q_{max}$: The adsorbent's monolayer adsorption capacity (mg/g).

$K_l$: The Langmuir affinity constant (L/mg) that is related to the adsorption energy

**Table 3.2**

*Langmuir model values*

| **Concentration** (ppm) Ci | **[$Pb^{2+}$] (ppm)** $C_f$ | **$q_e$** | **$1/c_e$** | **1/q** | **[$Cu^{2+}$] (ppm) $C_f$** | **$q_e$** | **$1/c_e$** | **1/q** |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.8840 | 0.348 | 1.13122 | 2.87356 | 0.754 | 0.246 | 1.32626 | 0.81300 |
| 5 | 3.9643 | 3.1071 | 0.25225 | 0.32184 | 2.27 | 2.73 | 0.44052 | 0.07326 |
| 10 | 6.9880 | 9.06 | 0.14326 | 0.11037 | 2.648 | 7.352 | 0.37764 | 0.02723 |
| 20 | 5.0521 | 44.8437 | 0.19793 | 0.0223 | 4.770 | 15.229 | 0.20963 | 0.01313 |
| 50 | 10.581 | 118.25 | 0.0945 | 0.0084 | 9.231 | 40.76 | 0.1083 | 0.00490 |

**Table 3.3**

*Langmuir Adsorption isotherms parameters for Carboxymethylated OISW*

| **Metal ion** | **Langmuir** | | | |
|---|---|---|---|---|
| | **$R^2$** | **$Q_{max}$** | **$K_1$** | **$R_1$** |
| **$Pb^{2+}$** | 0.9922 | 2.701 | 2.851 | 1.00 |
| **$Cu^{2+}$** | 0.9552 | 1.228 | 3.544 | 1.00 |

From the results in table 3.2, and figure 3.9 at appendix B it is obviously that R = 1, which means the adsorption is favorable since $R^2$ value is closed to 1, and the adsorption obeys Langmuir model.

### 3.9.2 Freundlich isotherm model

Freundlich isotherm model discusses and describes, the multilayer adsorption, and adsorption processes on heterogonous surfaces. If the figure 3.10 at appendix B ln(q) vs ln(c) gives a straight line with $R^2$ value closed to 1, then the adsorption obeys this model.

The Freundlich isotherm has the following linear form:

$$\ln q_{e} = \ln K_f + 1/n \ln C_e \qquad \text{Eq .8.3}$$

Where;

**$K_f$** is the Freundlich constant, which is related to the adsorption capacity (mg/g).

The heterogeneity coefficient (g/L) is denoted by the letter **n**.

**Table 3.4**

*Freundlich model values*

| **Conc (ppm)Ci** | **$[Pb^{2+}]$ (ppm)$C_f$** | **$q_e$** | **Ln $c_e$** | **Ln $q_e$** | **$[Cu^{2+}]$ (ppm)$C_f$** | **$q_e$** | **Ln $c_e$** | **Ln $q_e$** |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.8840 | 0.348 | -0.1233 | -1.05555 | 0.754 | 0.246 | -0.28236 | 0.207014 |
| 5 | 3.9643 | 3.1071 | 1.377329 | 1.13369 | 2.27 | 2.73 | 0.81978 | 2.61374 |
| 10 | 6.9880 | 9.06 | 1.943049 | 2.203869 | 2.648 | 7.352 | 0.973805 | 3.60441 |
| 20 | 5.0521 | 44.8437 | 1.619804 | 3.803183 | 4.770 | 15.229 | 1.562367 | 4.332699 |
| 50 | 10.581 | 118.25 | 2.359117 | 4.772845 | 9.231 | 40.76 | 2.222578 | 5.317357 |

**Table 3.5**

*Freundlich Adsorption Isotherms parameters for Carboxymethylated OISW*

| **Metal ion** | **Freundlich** | | |
|---|---|---|---|
| | **$R^2$** | **n** | **$K_f$** |
| $Pb^{+2}$ | 0.815 | 1.040 | 8.872 |
| $Cu^{+2}$ | 0.9682 | 1.731 | 7.855 |

From table 3.5 and (figure 3.10 at appendix B) since the plot of ln Ce/ln qe is not liner so the adsorption proses reaction does not match with Freundlich isotherm. The adsorption reaction using OISW polymer obey Langmuir isotherm for both ions.

### 3.10 Adsorption kinetics

To understand the adsorption process mechanism, the adsorption must be studied kinetically, by monitoring the adsorption speed, and whether affected by the conditions mentioned. Adsorption kinetic models were used to analyze adsorbent efficiency and analyze adsorption mass transfer mechanisms. To explain how metal ions are adsorbed, the results of applying kinetic principles such as pseudo-first order and pseudo-second order must be analyzed [77].

#### 3.10.1 pseudo-first order model

$$\ln (qe - qt) = \ln qe - K_1 t \qquad \text{Eq 9.3}$$

$K_1$: the first-order rate constant ($min^{-1}$)

$q_e$: the equilibrium amount of solute adsorbed per unit weight of adsorbent (mg/g).

$q_t$: the amount of solute adsorbed per unit weight of adsorbent at any given time (mg/g).

If the figure ln(qe-qt) vs time gives straight line with high $R^2$ value, then the adsorption obeys this model.

Table 3.6 and table 3.7 at appendix A were studied in addition to figure 3.11 at appendix B in order to see if the reaction obey this model or not.

#### 3.10.2 Pseudo-second order model

$$t/q_t = 1/k_2 q^2_e + t/q_e \qquad \text{Eq 10.3}$$

$K_2$: the second-order rate constant (g $mg^{-1}$ $min^{-1}$)

$q_e$: the equilibrium amount of solute adsorbed per unit weight of adsorbent.

$q_t$: the amount of solute adsorbed per unit weight of adsorbent at any given time.

If the plot $t/q_t$ vs time gives straight line with $R^2$ value approached, then the adsorption will obey this model.

Table 3.8 and table 3.9 at appendix A in addition to figure 3.12 at appendix B were studied.

From correlation coefficients ($R^2$) values of pseudo-first and second order the adsorption of lead ion on Carboxymethylated OISW seems to obey pseudo-second order since ($R^2 = 0.9978$) in this case is higher than ($R^2 = 0.8168$) obtained by applying in the first order. Also for copper ion the adsorption on Carboxymethylated OISW obeys pseudo-second order since ($R^2 = 0.9932$).

### 3.11 Adsorption Thermodynamics

Thermodynamic studies are also significant issue for studying adsorption, and so these studies were performed at various temperatures for thermodynamic purposes, and the calculated parameters included enthalpy ΔH, entropy ΔS and Gibbs free energy change ΔG. Also measured thermodynamic parameters such as temperature equilibrium constant, are important design factors. These parameters determine the spontaneity and feasibility of the process, and by applying the Van't Hoff plot's thermodynamic equation. The slope and y-intercept of the graph In ($K_{d)}$ versus (1/T) can be used to calculate the thermodynamic parameters (ΔH° and ΔS°) of lead ion, copper ion absorption on Carboxymethylated OISW.

After thermodynamic value for Vant Hoff plots were summarized at table 3.10 at appendix A ,and a figure 3.13 at appendix B were studied, Table 3.11 at appendix A Shows that the adsorption of both metal ion lead and copper on Carboxymethylated OISW is spontaneous since all ΔG° values are negative, a spontaneous process is one that occurs without the addition of external energy, also the entropy ($\Delta H° < 0$), so the process is exothermic, and hence inexpensive reaction. Finally, since ($\Delta S° < 0$), this give us an indication that the reaction is spontaneously occurs at low temperature, and this matches with our result that the maximum adsorption occurs at 20 $^{o}$C.

### 3.12 Wastewater Purification

As we mentioned before (sec. 2.10) a real sample of wastewater was used in order to determine the efficiency of the Carboxymethylated OISW toward the heavy metal ions removal. Table 3.12 at appendix A shows the concentration of heavy metals before and after the extraction prosses. The Carboxymethylated OISW shows a high efficiency for the harmful metal ions with high concentrations such as Al, Bi, Na, in addition to Pb, Cu with 60.00%, 93.00%, 86.00%, 87.00%, 94.00%, respectively, and other ions. Also,

Carboxymethylated OISW Showed highly sensitivity to even low concentration of ions, such as Cr, Te, Ti with 79.00%, 93.00%, 100.00% respectively and other harmful ions.

### 3.13 Conclusion

In this work, OISW was purified using acid wash techniques and Soxhlet extraction, then was successfully derivatized with ionic functional group by reacting it with sodium chloroacetate in alkali medium. In order to synthesis natural base, low cost derivatized OISW using CMC reaction. The carboxymethylated polymer was thermally cured, the curing leads to the formation of ester linkages between carboxymethylated OISW components. The cured product is a 3D polymer with various binding sites for metal ions. It showed very high thermal stability and was insoluble in water. The cured polymer was characterized by IR, TGA, and AFM instruments before thermal treatment and after. Concentration, dosage, contact time temperature, and pH Parameters was exanimated in order to investigate the adsorption optimum condition.

The 3D polymer was then used in purification of contaminated wastewater using optimum conditions determined using the model ions Cu(II) and Pb(II). The adsorption efficiency was good to excellent for multi elements present in a real sample of wastewater. The optimum value of the studied parameters for Pb(II) was about 30.00 mg dosage, 50.00 ppm concentration, pH value of 6, temperature 20 $^{o}$C , and a contact time of 60.00 min. For Cu(II) the optimum condition was 50.0 mg adsorbent dose, 50.00 ppm concentration, a pH of 6.00, a temperature of 20 $^{o}$C, and 60.00 min contact time.

The highest efficiency of removal was about 93.00% for copper (II) and 85.00% for lead(II), an application for toxic ion removal efficiency for a real sewage sample was determined, showing excellent removal for most of the metals present was attained. The reaction isotherm, kinetically, and thermodynamically also studied, and results showed that the equilibrium reaction with copper obeys pseudo-second order and for lead obeys pseudo-second order. Regarding the reaction isotherm, copper ions obeys Langmuir model which means that the adsorption reaction occurs not only on the polymer surface, but also inside the polymer structure. Process of removal of lead ion obeys Langmuir model two. The thermodynamic results show that the adsorption of both metal ion lead(II) and copper(II) on carboxymethylated OISW is spontaneous.

## 3.14 Recommendations

- Increasing active sites in order to increase the removal efficacy by adding more of the sodium chloroacetate.

- Icreasing surface area of the polymer by using Nano-scale technique.

# List of Abbreviations

| Abbreviation | Meaning |
|---|---|
| OILW | Olive Industry Liquid Waste |
| CMC | Carboxy Methylation Reaction |
| WHO | World Health Organization |
| BOD | Blood Oxygen Demand |
| OISW | Olive Industry Solid Waste |
| $R^2$ | Correlation coefficient (regression coefficient, fitting coefficient) |
| ICP-MS | Inductively Coupled Plasma Mass Spectrometry |
| FAAS | Flame Atomic Adsorption Spectrometer |
| AFM | Atomic Force Microscope |
| $q_e$ | The mass of adsorbate adsorbed per unit mass of adsorbent at Equilibrium(mg/g) |
| Cf | final concentration of metal ions in the sample solution (mg/L) |
| Ci | Initial concentration of metal ions in the sample solution (mg/L) |
| qt | Amount of adsorbate per unit mass of adsorbent at time t (min) |
| $K_1$ | The pseudo-first order rate constant |
| $K_2$ | The pseudo-second order rate constant |
| $K_f$ | Freundlich constant |
| $K_l$ | Langmuir isotherm constant (L/mg) |
| 1/n | Dimensionless Freundlich constant that indicate favorable of Adsorption pross |
| kd | The thermodynamic gas constant |
| $R_l$ | Dimensionless constant separation factor |
| ΔG° | The change in Gibbs free energy |
| ΔS° | The change in entropy |
| ΔH° | The change in enthalpy |

| | |
|---|---|
| R | The universal gas constant |
| T | The Absolut temperature |
| DS | Degree of substitutions |

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# Appendices

## Appendix A

## Tables of Study

**Table 3.6**

*Pseudo-first order model values*

| Time(min) | $[Pb^{2+}]$ cf | qt (mg/g) | Ln(qe-qt) qe=118.2552 | $[cu^{2+}]$ cf | qt (mg/g) | Ln(qe-qt) qe=203.8445 |
|---|---|---|---|---|---|---|
| 1.0 | 16.9125 | 6.6175 | 4.715259 | 15.2523 | 6.94954 | 5.28267 |
| 10.0 | 15.4064 | 6.91872 | 4.712557 | 13.6583 | 7.26834 | 5.28105 |
| 20.0 | 14.96 | 7.008 | 4.711755 | 10.7825 | 7.8435 | 5.27812 |
| 30.0 | 10.787 | 7.8426 | 4.704224 | 9.1745 | 8.1651 | 5.276478 |
| 60.0 | 10.2781 | 7.94438 | 4.703302 | 3.5976 | 9.28048 | 5.270761 |

**Table 3.7**

*Adsorption kinetic parameters (pseudo-first order model) for the adsorption of $Pb^{2+}$, $Cu^{2+}$ on Carboxymethylated OISW.*

| Metal ion | Adsorption kinetic pseudo-first order model | | | |
|---|---|---|---|---|
| | $R^2$ | Theo. $q_e$ | Exp. $q_e$ | $K_1$ |
| $Pb^{2+}$ | 0.8168 | 118.2552 | 108.994 | 0.0002 |
| $Cu^{2+}$ | 0.9949 | 203.8445 | 30.0120 | 0.0012 |

**Table 3.8**

*Pseudo-first order model values*

| Time(min) | $[Pb^{2+}]$ cf | qt (mg/g) | t/qt | $[cu^{2+}]$ cf | qt (mg/g) | t/qt |
|---|---|---|---|---|---|---|
| 1.0 | 16.9125 | 6.6175 | 0.151114 | 15.2523 | 6.94954 | 0.143894 |
| 10.0 | 15.4064 | 6.91872 | 1.445354 | 13.6583 | 7.26834 | 1.37583 |
| 20.0 | 14.96 | 7.008 | 2.853881 | 10.7825 | 7.8435 | 2.549882 |
| 30.0 | 10.787 | 7.8426 | 3.825262 | 9.1745 | 8.1651 | 3.674174 |
| 60.0 | 10.2781 | 7.94438 | 7.552509 | 3.5976 | 9.28048 | 6.465183 |

**Table 3.9**

*Adsorption kinetic parameters (pseudo-second order model) for the adsorption of $Pb^{2+}$, $Cu^{2+}$ on Carboxymethylated OISW*

| Metal ion | Adsorption kinetic pseudo-second order model | | | |
|---|---|---|---|---|
| | $R^2$ | Theo. $q_e$ | Exp. $q_e$ | $K_2$ |
| $Pb^{2+}$ | 0.9978 | 118.2552 | 9.478 | 0.0899 |
| $Cu^{2+}$ | 0.9932 | 203.8445 | 15.495 | 0.0394 |

**Table 3.10**

*Thermodynamic value for Vant Hoff plots.*

| Temp $C^o$ | $[Pb]^{2+}$ (ppm) | 1/T ($K^{-1}$) | ln kd qe=118.2552 | $[Cu]^{2+}$ (ppm) | 1/T ($K^{-1}$) | ln kd qe=40.7689 |
|---|---|---|---|---|---|---|
| 15 | 16.7322 | 0.003472 | 1.95551 | 13.0532 | 0.003472 | 1.138886 |
| 20 | 9.1681 | 0.003413 | 2.557115 | 2.3210 | 0.003413 | 2.865921 |
| 30 | 10.9456 | 0.0033 | 2.379907 | 5.0120 | 0.0033 | 2.096084 |
| 40 | 17.5542 | 0.003195 | 1.907552 | 8.9790 | 0.003195 | 1.513031 |
| 60 | 28.4532 | 0.003003 | 1.424584 | 17.0843 | 0.003003 | 0.86976 |

**Table 3.11**

*Adsorption of $Pb^{2+}$,$Cu^{2+}$ , on Carboxymethylated OISW thermodynamic parameters*

| **Metal ion** | **Temp.(K)** | **Adsorption Thermodynamics** | | |
|---|---|---|---|---|
| | | **ΔG° (KJ/mol)** | **ΔH° (KJ/mol)** | **ΔS° (KJ/mol.K)** |
| **$Pb^{2+}$** | 288 | -5.7094 | -14.433 | -0.03029 |
| | 293 | -5.5580 | | |
| | 303 | -5.2551 | | |
| | 313 | -4.9522 | | |
| | 333 | -4.3464 | | |
| **$Cu^{2+}$** | 288 | -5.0781 | -18.0122 | -0.04491 |
| | 293 | -4.8535 | | |
| | 303 | -4.4044 | | |
| | 313 | -3.9553 | | |
| | 333 | -3.0571 | | |

**Table 3.12**

*Results of analyses for hazardous metal concentration using Carboxymethylated OISW polymer by ICP*

| Metal ion | Initial Metal ions Concentrations [(ppm) | Final Metal ions Concentrations (ppm) using 50 mg Adsorbent | Removal (%) | Final Metal ions Concentrations (ppm) using 30 mg Adsorbent | % adsorption |
|---|---|---|---|---|---|
| Ag | 0.019 | 0.015 | 21% | 0.001 | 94% |
| Al | 7.668 | 3.042 | 60% | 3.094 | 59% |
| As | 0.624 | 0.282 | 54% | 0.360 | 42% |
| B | 11.330 | 6.236 | 44% | 7.131 | 37% |
| Bi | 7.176 | 0.478 | 93% | 0.527 | 92% |
| Cr | 1.538 | 0.322 | 79% | 0.741 | 51% |
| Cu | 14.774 | 0.825 | 94% | 0.923 | 93% |
| Fe | 23.753 | 22.787 | 4% | 16.671 | 29% |
| Mo | 0.515 | 0.232 | 54% | 0.192 | 62% |
| Na | 38857.980 | 5397.351 | 86% | 14879.767 | 61% |
| Ni | 0.484 | 0.342 | 29% | 0.308 | 36% |
| Pb | 11.805 | 3.787 | 68% | 1.550 | 87% |
| Te | 0.547 | 0.037 | 93% | 0.047 | 91% |
| Ti | 0.010 | 0.001 | 100% | 0.001 | 100% |
| U | 0.091 | 0.072 | 20% | 0.07 | 23% |
| V | 1.494 | 0.535 | 64% | 0.90 | 39% |
| Zn | 9.094 | 9.012 | 0.9% | 6.25 | 31% |

## Appendix B

## Figures of Study

**Figure 3.4**

*Carboxymethylated OISW dosage Effect on adsorption Pb(II) and Cu(II) ions*

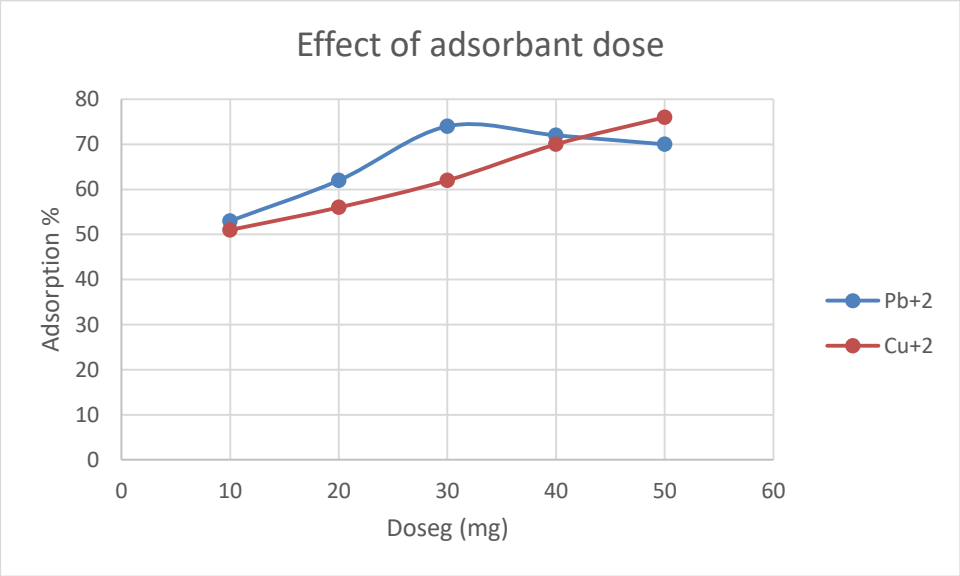



**Figure 3.5**

*Effect of metal ion concentration on adsorption*

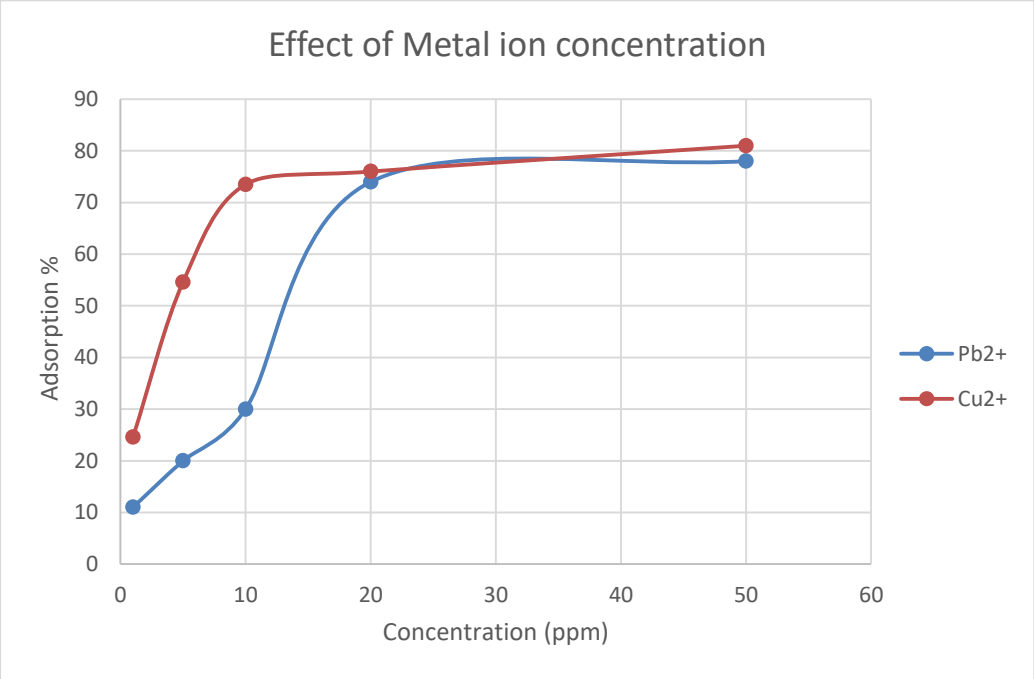


**Figure 3.6**

*Effect of contact time*

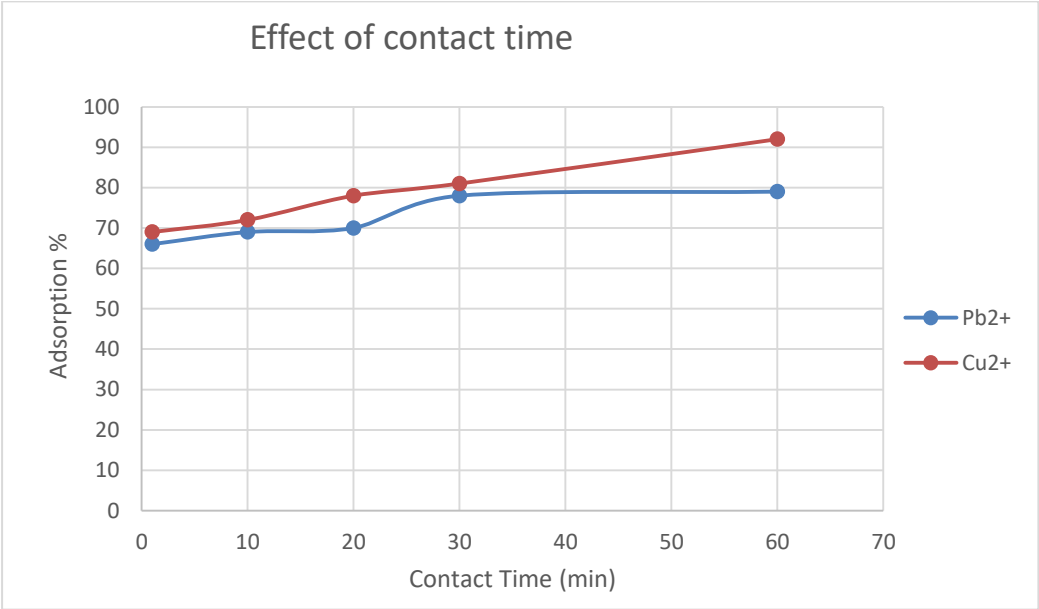



**Figure 3.7**

*Absorbance changes with temperature*

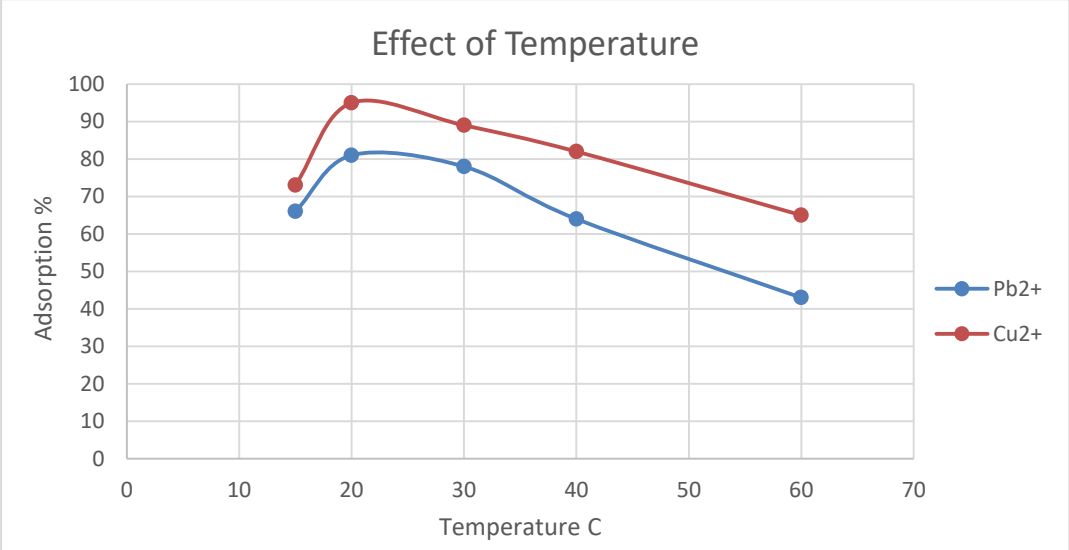


**Figure 3.8**

*Effect of pH on adsorption prosses*

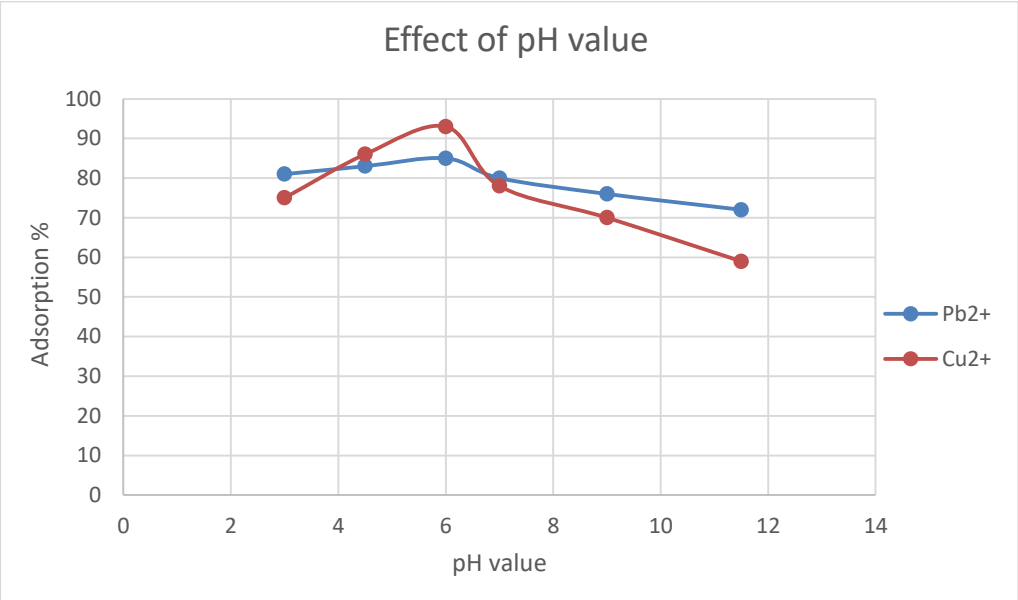



**Figure 3.9**

*Adsorption of Pb(II) and Cu(II) on Carboxymethylated OISW Langmuir model*

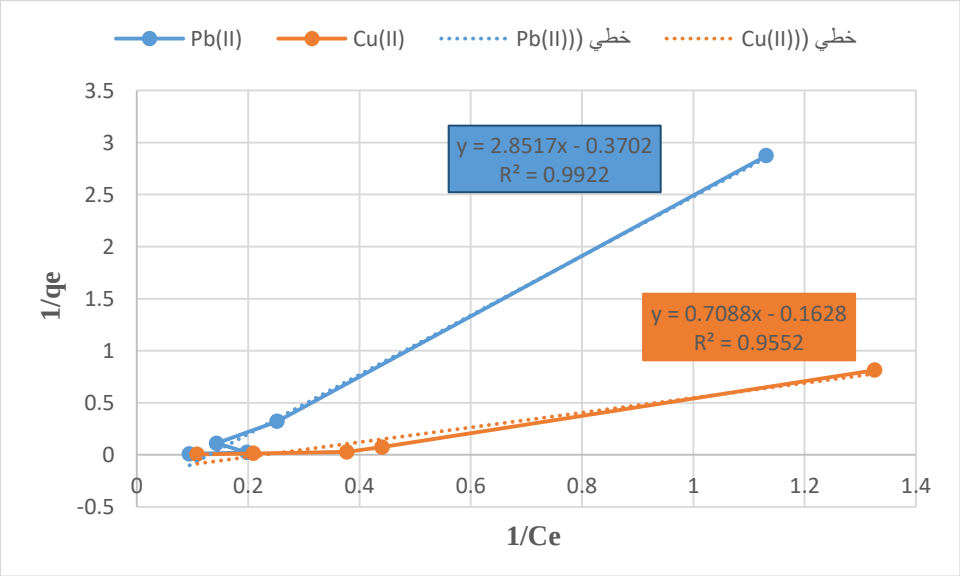


**Figure 3.10**

*Adsorption of Pb(II)and Cu(II) on Carboxymethylated OISW Freundlich model*

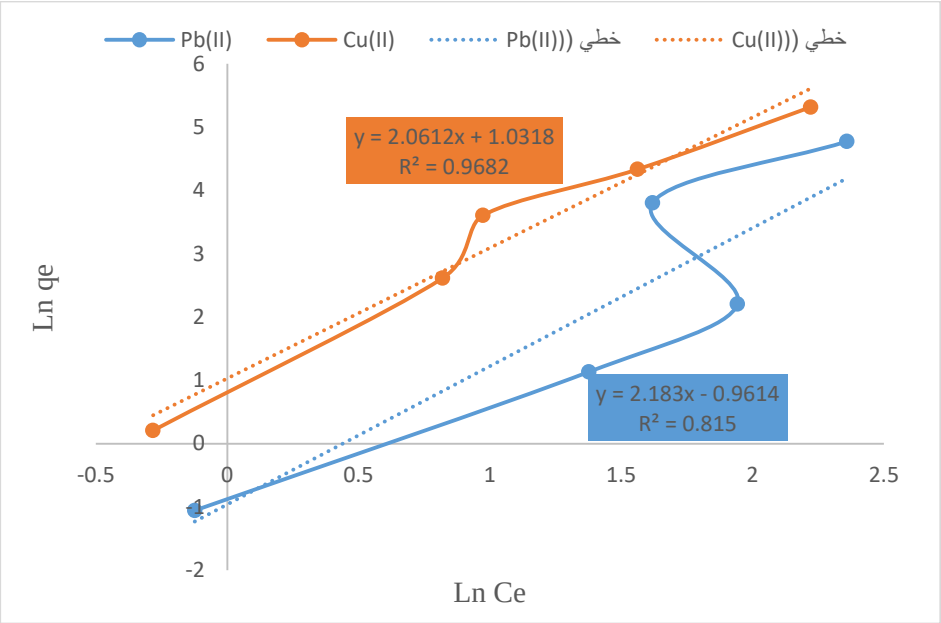



**Figure 3.11**

*Pseudo-first order model for the adsorption of $Pb^{2+}$, $Cu^{2+}$ on Carboxymethylated OISW*

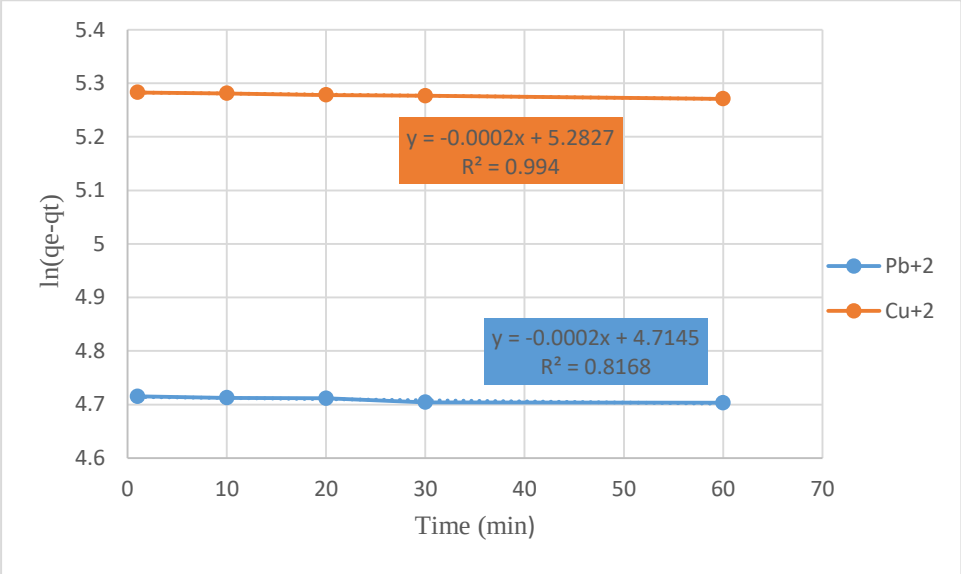


**Figure 3.12**

*Adsorption of $Pb^{2+}$, $Cu^{2+}$ on Carboxymethylated OISW Pseudo-second order model*

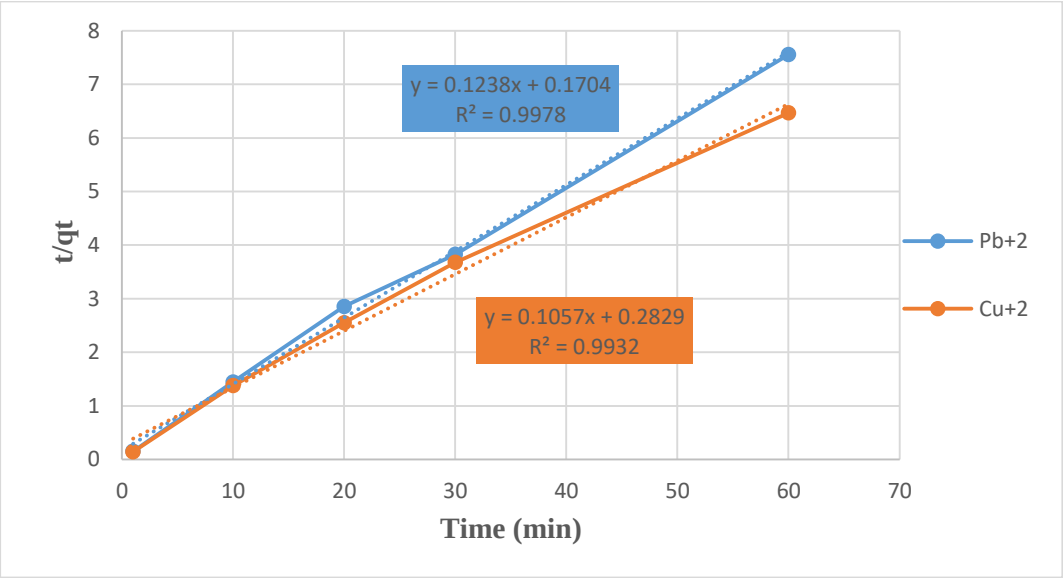
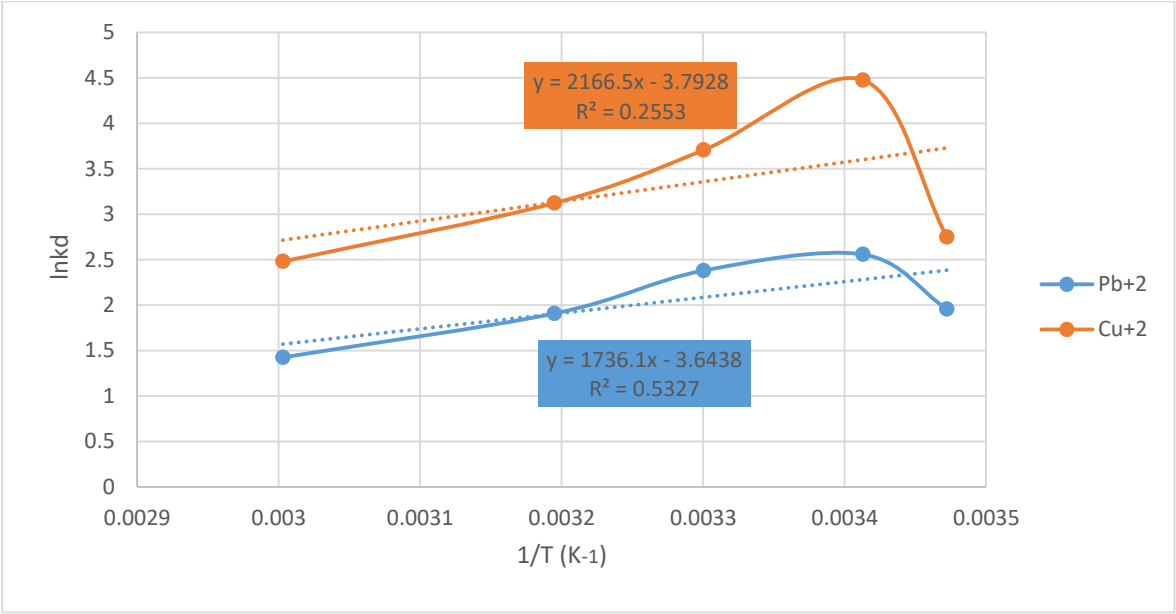



**Figure 3.13**

*Adsorption of $Pb^{2+}$ and $Cu^{2+}$ on Carboxymethylated OISW Van't Hoff plot*



جـامعـــة النجاح الوطنية

كليـــة الدراســـات العليـــا

# تحضير بوليمر من مخلفات الزيتون الصناعية (الجفت) بخصائص ايونية ومعالجته حرارياً واستخدامه في تنقية المياه العادمة من المعادن السامة

إعداد

أنغام جمال صلاحات

إشراف

أ.د. عثمان حامد

د. هشام قرارية

قدمت هذه الرسالة استكمالا لمتطلبات الحصول على درجه الماجستير في الكيمياء من كلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس– فلسطين.

2022

**تحضير بوليمر من مخلفات الزيتون الصناعية (الجفت) بخصائص ايونية ومعالجته حرارياً واستخدامه في تنقية المياه العادمة من المعادن السامة**

**اعداد**

**أنغام جمال احمد صلاحات**

**اشراف**

**أ.د.عثمان حامد**

**د.هشام قرارية**

## الملخص

**الخلفية:** يعد الماء اهم مصدر للحياة على سطح الأرض، للأسف مع تزايد عدد السكان وزيادة العمليات الإنتاجية والصناعية وقلة الاهتمام بالموارد الطبيعية، تخطى تلوث المياه الحد. تلوث المياه بالمعادن الكيميائية الثقيلة والسامة الناجمة من مصادر صناعية وزراعية، أحد اهم المشاكل العالمية التي يسعى لمعالجتها وإيجاد حلول للحد من اثارها العلماء ومنظمة الصحة العالمية. معالجة مبلمرات طبيعية موجودة بإضافة مواقع فعالة كيميائيا عليها هو أحد ابسط الحلول واقلها تكلفة واكثرها إنتاجية مع فعالية كبيرة لامتصاص المعادن السامة.

**الهدف:** الهدف من هذه الدراسة هو ابتكار طريقة غير مكلفة لتحضير بوليمر معدل جديد من مخلفات الزيتون الصناعية الصلبة (الجفت) واستخدامه في معالجة المياه من عنصري الرصاص والنحاس.

**المنهجية:** تنقية وتنظيف مادة الجفت من كل الشوائب والزيوت المصاحبة لها من خلال أكثر من طريقة، بداية مع تنظيف الجفت باستخدام الغسيل الحمضي له، ثم طريقة استخراج سوكلت للتخلص من الزيت المتبقي في الجفت. بعد ذلك يتم إضافة هايدوكسيل ميثيل على المواقع النشطة في الجفت باستخدام تفاعل الكاربوكسي ميثيليشن. علما ان الجفت يحتوي على السيليولوز والسيليولوز البدائي واللغنيين. ثم تتم معالجته حراريا وانشاء رابطة كيميائية جديدة وبوليمر جديد من نوعه. وتم فحص وتحليل البوليمر الناتج باستخدام TGA, FT-IRو AFM وتم فحص نشاط البوليمر وقدرته على امتصاص أيونات الرصاص ($Pb^{+2}$) والنحاس( $Cu^{+2}$) وتم فحص العوامل التي تؤثر على عملية الامتزاز مثل كتلة المواد الماصَّة وتركيز أيونات المعادن في المحلول المائي ودرجة الحرارة ودرجة الحموضة

والوقت. حيث أنه من خلال تجارب مختلفة تم اختيار أفضل الظروف وانسبها لتكون عملية الامتزاز وكفاءة البوليمر في اعلى مستوى.

**النتائج:** اظهر البوليمر الناتج نتائج مميزة في امتصاص وتنقية عنصري الرصاص والنحاس من المياه بنسب عالية، حيث انه تم امتصاص 85% من عنصر الرصاص بوجود 30 ميليغرام من البوليمر ودرجة حموضة 6 ودرجة حرارة 20. أيضا تم امتصاص 93% من عنصر النحاس بوجود 10 ميلغرام من البوليمر ودرجة حموضة 6 ودرجة حرارة 20.

**الخلاصة:** تم تقييم كفاءة الامتزاز للبوليمر على عينة مياه عادمة حقيقية ونجح في امتصاص الكثير من المعادن السامة بنسب عالية. تتميز عملية تحضير هذا البوليمر ببساطتها وقلة تكلفتها وفعاليتها.

**الكلمات المفتاحية:**

بوليمر؛ تلوث المياه؛ تنقية المياه؛ الجفت؛ الرصاص؛ عملية الامتزاز؛ المعادن الثقيلة؛ النحاس.