An-Najah National University

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THERMALLY BONDED COMPOSITE FORM PALM TREE WASTES: PRPEARTION AND APPLICATION IN WASTEWATER PURIFICATION FROM TOXIC METALS

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Dedication

I dedicate this thesis to: My beloved and supportive family All my teachers who provided me with vital information throughout my studies.

Everyone who has helped, supported, and encouraged me during my studies, even with a word of kindness. I dedicate this piece to my injured homeland, hoping to provide more than just this for each child impacted by the recent atrocities against Gaza. Additionally, I extend this dedication to my mom , siblings, educators, and those who contributed to shaping who I am today. I dedicate this work to my resilience during rough times, turning them into positive moments that influenced my future. I appreciate all the circumstances that enabled me to pursue my Master’s degree.

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Al-Najah national university represented by chairman of the department and lecturers'

doctors, and laboratory technician, I sincerely thank my family for their help, prayers, and support throughout my academic career.

Declaration

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

THERMALLY BONDED COMPOSITE FORM PALM TREE WASTES: PRPEARTION AND APPLICATION IN WASTEWATER PURIFICATION FORM TOXIC METALS

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.

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Date: 10/6/2024

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Abstract

Water is crucial for life on earth planet. Excessive inorganic and organic chemicals used in varies sectors such as agriculture, industry, household or other, can make the situation worse regarding pollutants in wastewater. Pharmaceuticals, paints, household chemicals, microorganisms, personal care products, plumbing chemicals, and other waste contaminants are common in sewage water. Heavy metal ions are among the most hurtful of these pollutants since they are nonbiodegradable and show long lasting effects, in addition to the high toxicity metals have even at ppm concentration. As a result, removing these hazardous heavy metal ions from water is becoming essential.

The main goal of this work is to develop a process for converting palm tree waste to value added material with ionic functional groups and use for removing toxic chemicals from wastewater.

Palm waste collected from Jerico areal in Palestine was ground, purified form soluble materials by Soxhelt extraction. The main three components of the waste are cellulose, lignin and hemicelluloses. All the three macromolecules have hydroxyl groups on their repeat units. The macromolecules were reacted as a mixture with sodium chloroacetate in an alkaline medium. The reaction introduced a carboxyl pendant on the three macromolecules. To reduce the extractives, the carboxymethylated polymers were thermally fused by heating them in an oven at 160 ^{o}C. The produced crosslinked composite was then used in wastewater purification form metal ions.

The Thermally cured composite was characterized using FT-IR and Scanning electronic microscopy (SEM). The FT-IR results indicate the formation of the target composite, and the SEM showed a porous structure with hollow fiber. The composite was used for removing toxic metal ions for contaminated water. The effect of various parameters such as initial metal ion concentration, pH, temperature, adsorbent dosage and contact time were studied as parameters affecting the adsorption of metal ions by the target polymer. Co(II) was used as a model ion, the highest metal ions removal was obtained at pH of 8 with a Co(II) concentration of 40 ppm, adsorbent dosage of 40 mg, and contact time of 30 min. The optimum extraction temperature was determined to be about 25°C. The adsorption process follows second-order adsorption kinetics model and thermodynamic study showed that the adsorption process is spontaneous and exothermic since as the temperature increases the absorption efficiency dropped.

Waste from palm tree was successfully converted to a composite with ionic functional group and used in removal of toxic metal ions from wastewater. The composite showed excellent efficiency toward all metal ions present in a real sample of wastewater.

Keywords: Carboxymethylated Cellulose; Cobalt(II); Heavy Metals; Palm Tree Waste.

Chapter One

Introduction

1.1 Background

The primary component of the earth, freshwater is necessary for all living things to survive. It provides nourishment, well-being, and vitality. Due to the lack of permanent lakes, lakes and insufficient rainfall, many nations worldwide—particularly those in desert regions like the Kingdom of Saudi Arabia (KSA)—are experiencing a water crisis. Due to its scarcity, water is becoming more and more precious in tandem with the world's population expansion [1].

In addition, millions of gallons of wastewater are added to freshwater reserves every day as a result of rising water demand in families, businesses, and agriculture. The UN estimates that the entire yearly volume of wastewater generated is about 1500 km^3, which is six times more water than there is in all of the world's rivers [2]. As a result of the untreated wastewater dumping, many freshwater lakes are becoming unfit for everyday use [3,4].

Wastewater from many sectors, including smelting, alloy manufacture, battery manufacturing, tanneries, paper production, radiator manufacturing, ceramics production, and mining, [3], One of the main sources of the many hazardous effluent types, which is growing in tandem with the fast expansion of industry, is textiles and dyes. [4]. Out of the many pollutants lurking in our water, both organic and inorganic, metallic ones are especially worrisome. These metals are super toxic and don't break down naturally, so they stick around in the environment for a long time. Among the worst offenders are cadmium, copper, platinum, lead, mercury, chromium, arsenic, and antimony [7, 8, 9, 10].

1.2 Contaminants of wastewater

One of the main things causing havoc with water safety and public health is the degradation of water quality. With the growing human population, the expansion of industrial and agricultural activities, and the possibility of climate change endangering the hydrological cycle, the declining quality of water has become a global problem [5].

Water specifications directly affect the quality of water in multiple ways. For example, unusable water in a certain region is effectively reduced when it is polluted and cannot be utilized for drinking, bathing, industrial, or agriculture. Although water quality is noted as a significant element in many countries, the water crisis is generally perceived as a problem regarding water amounts and quality [6].

In recent years, the loss of beneficial usage has also been used to calculate the contribution of dirty water to the water problem. that is, water lost to excessive bacterial, nutrient, metal, organic matter, salinity, and other toxic waste contamination that could have been used for good human, agricultural, and ecological purposes [7].

Waterborne illness transmission has previously established a strong connection between poor water quality and public health issues. In many developing nations, including Africa, this is a well-known problem [8].

About 80–90% of the heavy metals found in influent wastewater accumulate in sewage sludge, which may have an impact on the sludge's final properties and treatment. Unfortunately, there is no absolute guarantee that heavy metals will be removed from wastewater treatment plants (WWTPs). This can result in secondary environmental degradation [9].

As a result, it is crucial to effectively safeguard the environment against sewage sludge pollution in the modern world. It is even more crucial to keep in mind that using sludge as a substrate or fertilizer for soil restoration is the best way to manage it. As an alternative to landfilling or incinerating, between 30% and 50% of sewage sludge in EU countries is used in agriculture [10].

It is important to remember that elevated levels of heavy metals in sewage sludge have the potential to contaminate crops, soil, and surface and ground water, which can have detrimental effects on all living things, including people and animals [11].

The ability to evaluate the level of sludge pollution is limited by the overall quantities of heavy metals, and there is no clear indication of the possible ecological damage that these substances may provide to the environment and living things. The reason for this is that the toxicity, mobility, and bioavailability of heavy metals are determined by chemical means that are impacted by their interactions and leaching with various elements in nature [12].

The three-step chemical sequential extraction procedure, that is the method known as Tessier, was proposed by the Community Bureau of Reference (BCR; currently the Standards, Measurements and Testing Programme) and is the most widely used method to identify the chemical forms of heavy metals in sewage sludge [13].

It is important to note that every alteration to the environmental parameters affects metal mobility and, consequently, their bioavailability, such as pH, redox potential (Eh), organic matter content (OM), etc. Furthermore, when exposed to the biological, chemical, and mechanical processes employed in WWTPs, heavy metals bonded to the sludge structure may also change [14].

Therefore, during the various stages of sludge processing, it is crucial to examine both total concentrations and chemical forms. This method yields a more accurate evaluation of the possible ecological risk that these components may represent. There aren't many studies in this field of study in the scientific literature as of yet, and the ones that are are largely focused on dewatered sludge [15].

1.2.1 Toxic metals in wastewater

Human health is at risk when harmful heavy metals leak into the environment, posing a serious threat to aquatic ecosystems and water quality [16]. In waste-water, effluent from industry, and sludge from sewage, trace elements like arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn) are known to be metallic pollutants [17].

In surficial environments, the most inorganic stable forms of As and Cr occur as inorganic oxyanions but are frequently referred to as cationic species, e.g., As(III), As(V), Cr(II), and Cr(VI) [18].

Toxic heavy metals must generally be removed, either completely or partially, from wastewater and contaminated water in order to protect human health and the environment and maintain the sustainability of ecosystems [19].

The World Health Organization has established maximum contaminant or permissible limits for As, Cu, Pb, Cd, Cr, Co, Hg, Ni, and Zn in drinking water at 0.01, 2.5, 0.05, 0.0030, 0.050, 0.100, 0.0010, 2.000, and 5.000 mg/L, respectively [20].

Chemical precipitation, lime coagulation, ion exchange, reverse osmosis, and solvent extraction are some of the conventional methods for removing metal ions from effluents. However, these methods have drawbacks, including low metal removal, high reagent and energy requirements, and the creation of waste products or toxic sludge that needs to be properly disposed of [20]. As a result, developing effective and eco-friendly techniques to lower the number of heavy metals is essential.

Drinking water contaminated with these heavy metals can lead to a range of health problems. These issues can include diarrhea, stomach troubles, mouth sores, tumors, problems with red blood cells, difficulty with coordination, paralysis, vomiting, and even seizures. It's important to note that each of these metals has its own unique way of causing harm. [21], the successful recuperation of overwhelming metals from squander streams is considered imperative. Major significance has been connected to the treatment of mechanical wastewater gushing, as nearby and universal specialists require that mechanical wastewater ought to be treated to meet a set standard some time recently released into water bodies.

The primary cause of organic waste and hazardous heavy metal pollution in water is the world's rapid expansion as related to the industrial operations. The dilemma gave rise to a significant environmental issue. The overabundance of metals in water sources could provide serious hazardous risks to both humans and animals [22, 23].

For example, cerebral retardation, attention deficit hyperactivity disorders, and neurobehavioral problems can all be brought on by mercury concentrations that are higher than allowed [24]. A nephrotoxic impact and bone deterioration can result from high cadmium concentrations [25]. Lead has also been linked to anemia, encephalopathy, behavioral abnormalities, cognitive decline, and renal damage [26].

Anorexia, weakness, lethargy, and gastrointestinal tract injury have all been linked to high copper concentrations [27]. Controlling environmental pollution now requires removing heavy metal ions from waste fluids before they enter water sources. Chemical precipitation, reverse osmosis, ion-exchange, membrane separation, coagulation and flocculation, adsorption, and biosorption are a few of the techniques that have been developed for this purpose [28].

1.3 Wastewater purification

1.3.1 Basic methods of water treatment

There are several strategies utilized in the water refinement handle, which incorporate:

1. Boiling water: boiling water is the cheapest and most secure strategy for water refinement. It destroys disease-causing living beings and is successful in removing parasites and germs.
2. Filtration water: Filtration is one of the successful ways of purifying water. It is effective for fundamental water tasks such as silt and chlorine removal1. Water treatment plants use different types of filters, such as sand, rock, and charcoal, to evacuate pollution from water.
3. Reverse Osmosis: is a water refinement strategy that removes particles from water. Water treatment plants regularly utilize reverse osmosis when treating reused water or salt water for drinking.
4. Refining: Refining is the process of changing a fluid into vapor to condense it back to fluid frame. It is utilized to remove debasements from water and is regularly utilized in mechanical applications.
5. Chemical Treatment: Chemical treatment is utilized to remove contaminants from water. Coagulation is regularly the primary step in water treatment, where chemicals with a positive charge are included into the water to neutralize the negative charge of earth and other broken-down particles in the water. Other chemicals, such as chlorine, are included to kill bacteria and viruses. It's critical to note that diverse strategies of water decontamination have their merits and demerits, and the appropriate method of refinement depends on the contaminants display within the water.

Chemical and microbiological examination is essential to decide the fitting strategy of purification water contamination can lead to the degradation of aquatic ecosystems, spreading water-borne maladies, and diminishing the environment administrations. The water asset would otherwise provide water poisons that may cause disease or act as harms. Numerous water toxins enter our bodies when we use water for drinking and food planning. Water contamination could be a major worldwide natural issue that can result in millions of passings and sicknesses each year. Water contamination is the defilement of water bodies, such as lakes, streams, seas, aquifers, supplies, and groundwater, more often than not as a result of human exercises. Water pollutants include chemicals, trash, bacteria, parasites, and perilous squander. Water contamination can lead to the corruption of aquatic ecosystems, spreading water-borne diseases, and decreasing the environment services that the water asset would something else give. Water toxins may cause infection or act as harms, and numerous water poisons enter our bodies when we utilize water for drinking and food preparation. Water contamination may be a major worldwide natural issue that can result in millions of passings and ailments each year. There are several sources of water contamination, counting sewage releases, mechanical exercises, rural exercises, and urban runoff, counting stormwater. Water pollution can be caused by harmful substances entering bodies, getting broken down in them, lying suspended in the water, or storing on the bed Water contamination.

This can be controlled through different measures, such as legitimate transfer of hazardous waste, decreasing the use of pesticides and fertilizers, and treating sewage before discharging it into water bodies. It's vital to note that water filtration strategies such as boiling and filtration work as it were to kill microbes or viruses from water, and not chemicals, oils, harmful substances, sewage, or other contaminants.

1.3.2 Advanced methods of water purification

Water quality is basic for human wellbeing. Be that as it may, as human action, populace development, and the utilize of chemicals in farming and mechanical advancement have all contributed to a decrease in water quality, different countries around the world will before long confront a deficiency of secure drinking water. Hence, finding approaches to improve water quality and decontaminate it from poisons was basic. Reusing wastewater may be a commonsense reply to this prerequisite since water is essential for life, and water utilization has always been rising to meet the developing requests of anthropogenic exercises and nourishment generation. Innovations for treating wastewater can be categorized as essential, auxiliary, and tertiary medicines. Through physical and chemical strategies, natural materials and suspended solids are evacuated from wastewater as portion of prompt treatment. When taking care of noteworthy levels of overwhelming metal defilement, the vital essential innovations incorporate microfiltration, chemical filtration, coagulation, and flocculation [29]. When looking at the methods used to purify the water that was mentioned previously, we find that they have many advantages and disadvantages, and among these disadvantages such as the formation of sludge, impact on the environment, high cost, difficulty in application, unselected, need other treatment, and incomplete treatment. [30]. Auxiliary cures depend on characteristic organisms that can break down natural and inorganic toxins into more secure, less difficult compounds (Within the nearness of oxygen, organisms change contaminants into carbon dioxide and modern biomass), expanding the evacuation effectiveness.

Although inquiries about the proficiency of organisms in evacuating metals is persistent, early comes about appear critical expulsion rates [31]. Chemical oxidation, electrochemical precipitation, crystallization, refining, photo-catalysis, adsorption, layer innovations, and particle trade innovations are a couple of. For an case of tertiary treatment, wastewater is changed into high-quality water at this point [31].

Adsorption is one of the superior ways to expel a extend of contaminants from water, counting overwhelming metals, as compared to past strategies:tall expulsion capacity, diminished vitality utilize, the capacity to dodge critical byproducts, proficiency, selectivity, cheap, and recyclability are many of its benefits [32].

1.3.2.1 Adsorption

The adsorption handles two categories, chemical adsorption, which happens when the adsorbent and adsorbate frame bonds by covalent and ionic bonds. In addition, physical adsorption happens due to electrostatic, such as van der Waals strengths [32].

When choosing any adsorbent, a set of characteristics must be taken into consideration, and among these characteristics [32].

High adsorption capacity: the sum of adsorbate retained by the adsorbent per unit mass depends on numerous components like temperature, concentration, and the porosity of the adsorbent.

Amazing selectivity: It is the selectivity of a substance or component in a arrangement compared to another.

Re-generable: To be important and suitable for commercial utilize, it must be substantial for a few benefits. And best energy: to progress the adsorption handle rate.

Consistent (solidness): Working variables, counting pH, temperature, and erosion, ought to not lead the adsorbent particles to deteriorate too much. In addition to the low cost, Stable thermally and chemically

1.3.2.2 Parameters that impact the absorption of heavy metal

Numerous impacts influence the adequacy of removing metals from contaminated water:

1. The foremost basic figure impacting the adsorption handle is the pH. In unbiased water or one with a lower pH, the metals are cationic and break down, though, at high pH, the adsorption of the metals is less proficient since anions and hydroxide are generated. Additionally, a move within the pH causes an alteration within the adsorbent's surface charge [33].
2. Temperature: Changing the temperature influences the adsorption efficiency, as in a few adsorbents, when the temperature increments, the adequacy of the adsorption prepares increments. This was deciphered as increasing the temperature, which expanded the adsorption sites [34]. A few adsorbents are adversely influenced by the rise in temperature since the temperature changes the pores of the absorbent [35].
3. Particles concentration: The nearness of particles and an increment in their concentration in water, such as chloride, diminishes the adequacy of adsorption since chloride creats a chloride complex, which is troublesome to remove from water since it contains a destitute partiality for adsorption [36].
4. Normal natural matter (NOM): The nearness of NOM within the water coming about from the deterioration of creatures and plants diminishes the adsorption of overwhelming metals since they have an acidic nature that makes a difference them connected with overwhelming components through a few strategies such as chelating and complex formation with overwhelming metals, which leads to changing their nature, poisonous quality and accessibility and their versatility [36].

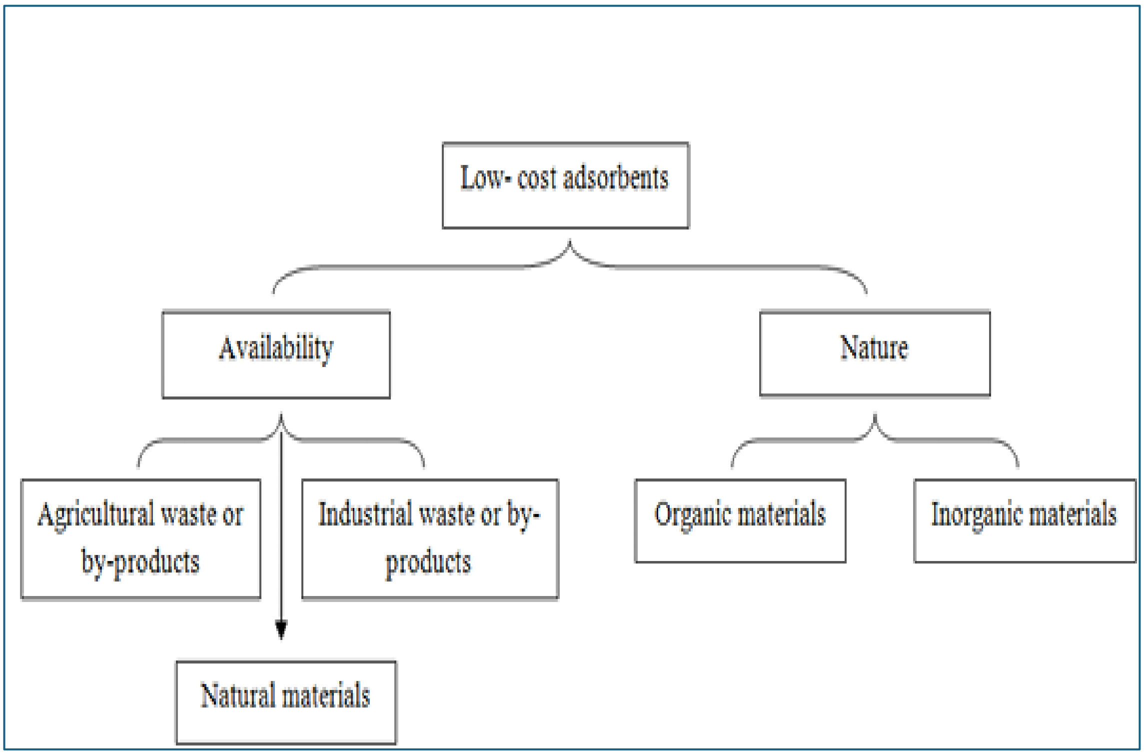
1.3.2.3 Materials used as adsorbent

Adsorbents can generally be divided into: Adsorbents derived from nature: Adsorbents of this kind are found in nature; examples include zeolites, clay minerals, charcoal, red mud, soil and silt, and ore minerals. They are readily available and inexpensive to acquire. Their adsorption capacity can be readily increased by modification [37]. Artificial adsorbents: These adsorbents are made from raw materials such polymeric adsorbents, industrial waste, agricultural waste, and sewage sludge, among others. In comparison to natural adsorbents, they are costly [37]. Every form of absorbent has unique qualities and attributes of its own. Adsorbents come in a variety of forms; some of the more widely used ones are molecular sieves, activated carbon, activated alumina, and activated clay [37].

According to Pollard [38], an adsorbent's cost is a crucial consideration when choosing one, as they are typically inexpensive and readily available in large quantities. As a result, efforts have been focused on creating affordable substitute adsorbents, and a wide range of materials have been studied in this regard. They can be categorized in two ways: (i) according to their availability, i.e., (a) natural material; (ii) according to their nature, i.e., (a) inorganic or (b) organic material [39]. Alternatively, they can be categorized according to where they are found.

Figure 1.1

Shows selected and possible classifications of low-cost adsorbents



Many materials were used in adsorption to eliminate pollutants and heavy metals, each with advantages and disadvantages.

1.3.3 Types of adsorbents

The most crucial characteristics of any absorbent are its cost, kinetics, compatibility, renderability, capacity and selectivity. Adsorbents can be based on organic material sources like inorganic materials like zeolites or activated carbon. Large specific surface area, consistent molecular-sized channel size, and high porosity are essential qualities of effective adsorbents. high ion exchange capabilities; High adsorption capacity across a broad range of adsorbate concentrations; high levels of catalysis and pore accessibility to facilitate the passage of some molecules during adsorption and the breakdown of others; simplicity, low operating costs, and a successful method; simple to regenerate and again use; high melting point, strong thermal stability, and resistance to dehydration in structure; little acquisition costs and does not.

1.3.3.1 Activated carbon (AC)

Actuated carbon is one of the foremost broadly utilized materials as an adsorbent to induce freed of overwhelming metals and poisons in watery media because it contains numerous pores. In expansion, it features a tall surface range, which may reach 3,000 m^2/g, and it can be prepared from numerous crude materials such as wood and coconut shells. Be that as it may, it endures from a high production fetched, making it not commercially reasonable. It too causes auxiliary contamination from filtering actuated carbon within the water [42].

1.3.3.2 Activated Alumina

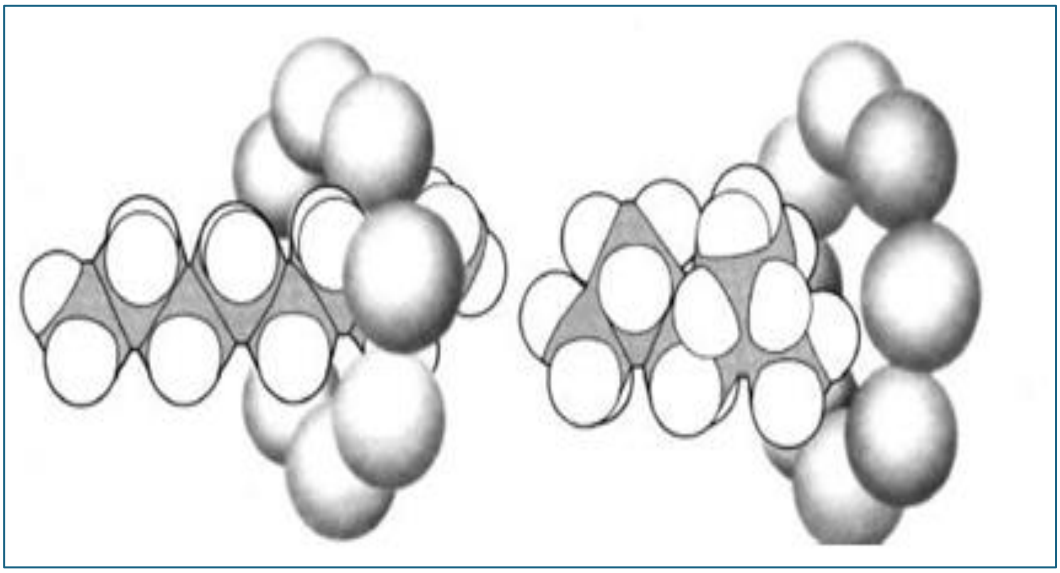
Aluminum oxide is the ingredient in activated alumina (Al_2O_3). Activated alumina. Bauxite ($Al_2O_3.3H_2O$) with significantly more than 200 m^2/g of specific surface area and high porosity usually is calcined under high temperature conditions to prepare it. According [43], activated alumina is most frequently utilized in a variety of adsorption and catalytic applications. For instance, it can be used as a desiccant to dry gases and as a filter to remove fluoride, arsenic, and selenium from drinking water.

1.3.3.3 Molecular sieves

Crystalline metal aluminosilicates, which are found in nature as adsorbents with enormous specific surface areas and very uniform pore sizes, are known as molecular sieves. As seen in figure 1.2, the adsorbent allows small molecules to flow through their pores and be adsorbed while preventing the passage of any larger molecules through them. Molecular sieves are employed as adsorbents in a variety of applications for the filtration of gases and liquids [49], as explains. Natural zeolites were employed in this work as adsorbents to extract naturally occurring heavy metals from the industrial effluent. The general features of zeolites are thoroughly covered in the upcoming chapter.

Figure 1.2

Zeolite sieve used in separation of the hydrocarbon octane from a branched isooctane



1.3.3.4 Industrial waste materials

Mechanical byproducts are materials that come from mechanical forms and are arranged of as squander. These materials get awesome consideration for utilize as adsorbents to channel water from overwhelming metals since they are reasonably and accessibility and exceedingly compelling in water refinement [44]. A case is coal fly fiery debris, a byproduct of coal combustion. It was utilized as an adsorbent within the removal of overwhelming metals such as cadmium(II) and nickel(II), and the adsorption capacity was 0.089 mg/g and 4.50 mg/g, respectively [45].

In expansion, lignin from mechanical squander from the paper generation handle was utilized as a retentive. It showed high effectiveness, because it was utilized as an adsorbent for cadmium(II) and copper(II), and the adsorption capacity was 0.226 mmol/g and 87.05 mg/g, individually [46]. In expansion, numerous mechanical squanders, such as slime [44] and slag [45, 46], were utilized as adsorbents. Be that as it may, the utilize of mechanical squander in water purification endures from the truth that it isn't appropriate for commercial utilize [44, 46].

1.3.3.5 Agro-waste as adsorbents

They are residual plants which have no financial advantage, they are too arranged of by burning, antagonistically influencing the environment. These buildups incorporate the leftovers of creatures and plants in strong or fluid shape. Subsequently, the scientist started utilizing these buildups to treat water and filter it from overwhelming metals. Moreover, other poisons, and the foremost critical of these buildups, are plant buildups, where these buildups get critical consideration, such as rice husks, sawdust, wood clean, and coconut husk since they comprise of cellulose, lignin, and hemicellulose, as these compounds have a tall capacity to adsorb overwhelming metals [44].

1.3.3.6 Composite adsorbents

These adsorbents comprise of two or more substances to extend their adequacy and soundness beneath extraordinary conditions and encourage their division. Cases incorporate the utilize of chitosan with silica to extend its stability beneath extraordinary conditions and Fe_3O_4 nanoparticles to extend the viability of adsorption; as chitosan alone had an adsorption of 0.082 mg/g, chitosan combined with silica and magnetite had an adsorption capacity of 1.699 mg/g, which is 20 times more prominent than alone chitosan. Besides, ease of division utilizing an outside attractive field [47].

This sort of adsorbent is characterized by expanding the adsorption capacity by increasing the surface range and hence expanding the dynamic locales. In any case, it endures from its reliance intensely on temperature and pH and in some cases causes contamination [48].

1.3.4 Natural based polymeric adsorbent

Among the most widely used natural based polymers are cellulose, lignin and chitosan.
In a published study, the solid waste of olive industry was carboxylate by reacting it with sodium hydroxide and sodium chloroacetate in isopropyl alcohol. The produced thermosetting composite was used as an adsorbent for metal ion in wastewater, high removal efficiency about [49].

In this 92% was attained toward most metals present in wastewater [43]. In this study we plan to use the waste collected from palm tree after modification as an adsorbent for toxic metal ion form wastewater.

1.3.4.1 Palm tree

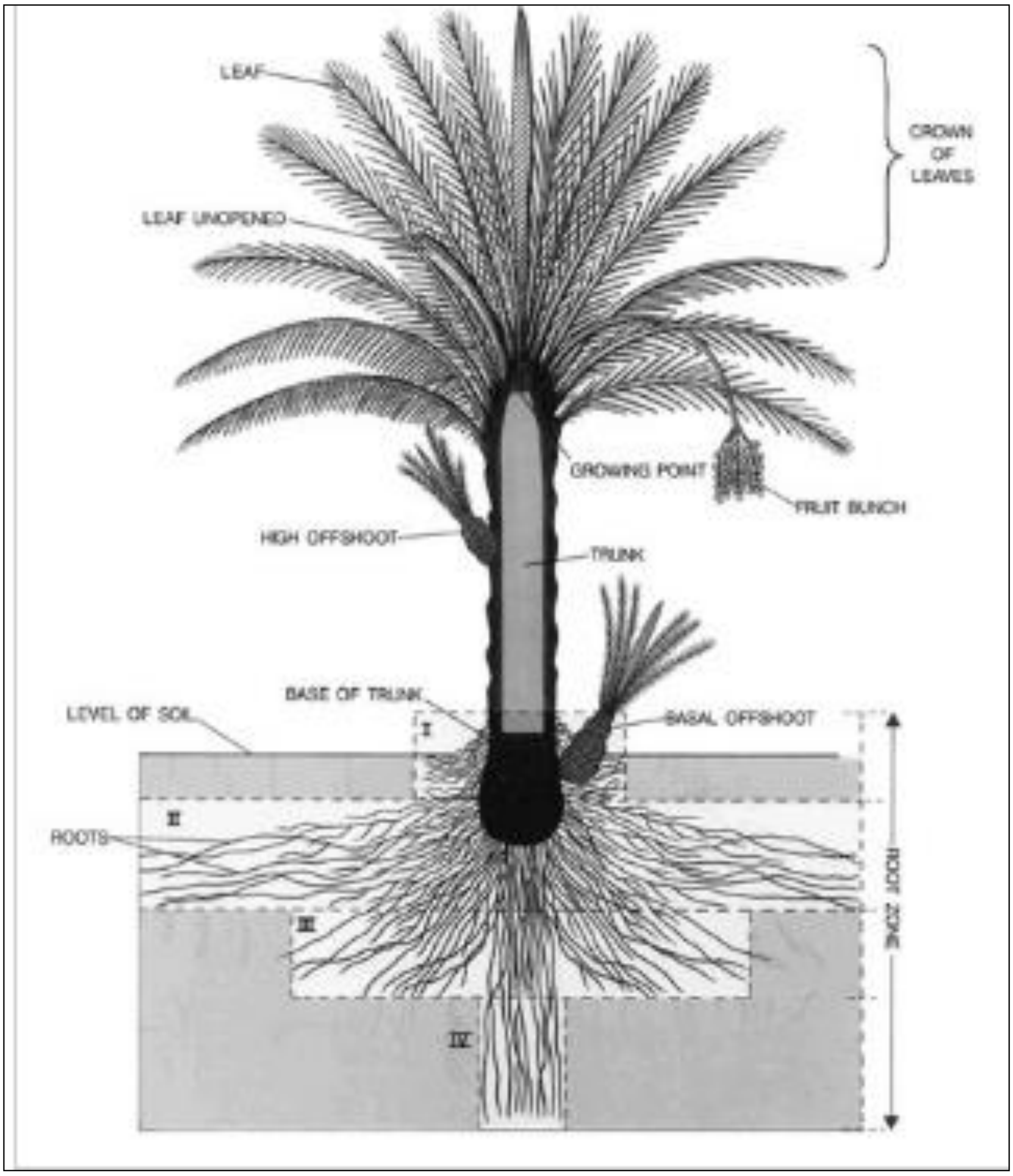
Palm tree is a type of evergreen plant belonging to the Aceraceae family (figure 1.3). It is considered one of the most widespread tree in the Middle East due to the suitable climate and its sweet fruit that is rich in nutrition [50].

The palm tree leaves are considered a renewable natural resource because it can be replaced in a relatively short period of time. Usually, date palm waste is disposed in landfills or burned on farms, which cause environmental pollution. The average economic life of a date is over 40 year, some of the trees are close to 50 years and still productive [51, 52]. The care for the palm includes removing of the offshoot, and dead or defective fronds every yearl, this generates about 20 kg of waste per year per palm tree. Some studies have reported that Palestine alone generates more than 50,000 tons of date palm biomass each year [53].

The waste products from date palms include leaves, bases of dry fronds, offshoots, and pits of dates. Local farmers say that they typically gather this debris and burn it. A portion of the trash is either left to decompose naturally and be used as fertilizer, or it is chopped up and combined with other bio waste to be fed to animals [52, 53]. Waste gathered from palm trees is burned or dumped untreated onto land or in water. However, these choices were detrimental to our economy over time as well as the environment in the long run due to the issue of global warming and massive garbage production. There is still no efficient waste management for palm trash. Although several research on the uses and byproducts of palm trash have lately been published, there is still a dearth of proper industrial utilization for these uses. The waste from palm trees is used to make composites [54,55], remove phenolic pollutants [56,57], and produce lactic acid and glucose [58].

Figure 1.3

Date palm tree schematic



Source: Jiménez-Cedillo, M.J., Olguín, M.T., Fall, C.Colin-Cruz, A. (2013).

A date garden's economic life spans from 40 to 50 years on average, but some can continue to produce for up to 150 years [28]. The date palm needs special attention throughout this period of life. A single date palm produces roughly 22 kg of garbage year when the branch is removed, and dead or damaged fronds are removed. According to certain research, Saudi country produces more than 200,000 tons of date palm biomass annually on its own [53].

Depending on the intended use, date palm waste industrialization necessitates a thorough examination of the mechanical and chemical characteristics in addition to specialized research on the mechanical qualities, nutrition, or pyrolysis analysis. Nevertheless, the date palm tree produces trash from a number of different parts. Date palm trees produce trash every year in the form of fronds, empty fruit bunches, date palm fiber, and dried fruit; dead palm trees produce garbage in the form of empty trunks; date palm seeds, also known as date stones or pits, produce waste from the date paste industries. [50].

1.3.4.2 Waste Chemical Composition

Because most of the palm trash is fibrous, chemical studies concentrate on the fiber. The relationship between chemical composition and several significant natural fiber properties, including biodegradability, recyclability, weather resilience, fungal attack, etc., highlights the significance of this field of study. These qualities are highly dependent on the chemical makeup [59]. Cellulose fibers ensconced in a lignin matrix make up the majority of plant fibers. The biostructure of palm fiber, which endows it with favorable mechanical qualities, is what sets it apart. The main wall of the building surrounds three minor walls at the beginning. Hemicelluloses make up each wall, and lignin serves as a matrix. On the outside of each wall, the cellulose molecules link up to produce a sequence of helically wound cellular micro-fibers [59]. In contrast to synthesis, it is evident that the palm fiber is hollow because of the lumen.

Table 1.1

Waste contents of palm tree

Constituents	cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Extractive (%)
Leaf	54.75	20	15.30	1.75	8.2
Leaflet	40.21	12.8	32.2	10.54	4.25
Rachis	38.26	28.17	22.53	5.96	5.08

Source: Zhu, B., Fan, T.Zhang, D. (2008).

As shown in Table 1, the waste mainly of cellulose fibers, lignin and hemicellulose [60]. Some of the physical properties of the fiber present in the waste are summarized in Table 2. In addition, the fibers are hollow, which makes it more porous and excellent adsorbent for metals.

Table 1.2

Physical properties of date palm fiber

Density(g/cm3)	0.9_1.2
Length(mm)	20_250
Diameter(Mm)	100_1000
Specific modulus(approx..)	7
Elongation to break(%)	2_19
Thermal conductivity(W/mK)	0.083

Source: Amin, M.T., Alazba, A.A. & Shafiq, M. (2015)

Palm fiber waste is valuable due to the huge diversity of its applications. Using of Palm tree wastes in Purification of toxic metals from waste water Cellulose, hemicellulose, and lignin are the main components of the cell wall of natural fibers [61, 62], thermally bonding of these components after derivatization could results on a value-added composite that is useful in waste water purification form toxic metals

1.4 Aim of the study

This work concern derivatizing the components of palm waste with carboxyl functional group and thermally fusing the components though and ester linkage then use the produced composite in waste water purification form toxic metal ions such as lead (II), Copper (II) and others.

The long-term objective of this work is to develop a process for making a composite with carboxyl functionality from the palm tree waste and using it in wastewater purification form toxic metal ions.

The sub-objectives comprise:

1. Functionalizing the components of the palm tree waste with carboxyl group.
2. Thermal bonding the functionalized components through an ester linkage.
3. Evaluating the possibility of using the prepared composite in wastewater purification.
4. Confirming the presence of the carboxyl functional group by FT-IR and other spectroscopic means.
5. Determining the degree of substitution by titration with NaOH (aq).
6. Determining the optimum adsorption efficiency by studying the effect of various factors such as, solution pH, solution temperature, metal ion concentration and mixing time on adsorption.
7. Performing a study on the mechanism of adsorption.
8. Developing a process for regenerating the absorbent.

Study will be conducted on Co (II) to determine optimum adsorption conditions. The obtained conditions then will be applied on areal sample of wastewater.

Chapter Two

Experimental

2.1 Materials and Methods

2.1.1 Material

All chemicals used in this research were of analytical grade and used as received. The chemicals were purchased from Sigma-Aldrich company (Jerusalem). The chemicals included sodium hydroxide, sodiumchloroacetate, and copper (II) nitrate. All prepared solutions were prepared using deionized water collected using a 18.2 MW cm Millipore (Millipore Corporation, Burlington, USA). Plam waste used in this project was collected from Jericho area (Palestine).

2.1.2 Methods

2.1.2.1 Characterization

The thermal behaviors of the CMPW and curing product were studied using the thermo-gravimetric analysis TG/DSC (Star System, Mettler-Toledo, OH, USA), heated at 10 $^{o}C.min^{-1}$ from room to 1100.0 ^{o}C. Obtained IR spectra were registered using a Fourier infrared spectrometer by Nicolet -6700 (Thermo-Fisher company, Waltham). The FT-IR was set at 4 cm^{-1} resolution. The obtained spectra were in the range of (600–4000) cm^{-1} with (64) scans. The final concentrations of studied ions Pb(II) and Cu(II) were determined using a flame atomic absorption spectrometer (FAAS, ICE3500 AA System, Thermo Scientific, UK). The quantitative and qualitative studies of wastewater were performed using inductively coupled plasma mass spectrometry (ICP-MS, CAPTM RQ ICP-MS, Thermo Fisher Scientific, Waltham, MA, USA). The average of three runs was provided for each analysis. The pH values of the aqueous solutions were determined using the pH electrode by Mettler-Toledo (Mettler-Toledo (Schweiz) GmbH).

2.1.2.2 Purification of palm waste

A 50.0 g sample of dried palm waste (PW) was ground by passing it through a Wiley mill fitted with a 20-mesh screen (ThomasWiley® Mini Cutting Mills, Swedesboro, NJ, USA). The ground PW was stirred in acidic solution with a pH of 3.5 (500 mL) for about 60 min to remove water-soluble extractives. The residue was then collected by vacuum filtration and washed several times with distilled water until the filtrate was neutral to litmus paper and clear. The collected PW was allowed to dry overnight at room temperature.

2.1.2.3 Soxhlet Extraction

Soxhlet extraction was performed on a ground sample of PW to remove residual organic extractives. The PW after washing as shown in the above experiment was placed in the Soxhlet extractor containing ethyl acetate (500 mL) and extracted for 2.0 h.
The collected sample of PW was dried in the hood and stored in a refrigerator for Future use.

Figure 2.1

Soxhlet Extraction

2.1.2.4 Carboxymethylation of PW (CMPW)

A 20.00 g sample of purified PW was added to a three-neck round bottom flask fitted with a magnetic bar, a thermometer, and a condenser attached to an oil bubbler. The PW samples were suspended in 250.00 mL of isopropyl alcohol. Then treated with 20.00 mL of 50.00% NaOH solution by dropwise addition over a period of 15 min. using a plastic syringe. The produced reaction mixture was stirred at room temperature for 10 min then 42.00 g (0.36 mol) of sodium chloroacetate solid was added in one portion. The flask contents were heated slowly to 65 ^{o}C in 1 hr and maintained at this temperature for another 1 hr. The reaction was stopped by the addition of 15.0 mL of glacial acetic acid. The solid was collected by vacuum filtration and washed four times.

with a methanol/water solution (3:2 ratio by volume). The last wash was performed with acetone. The mass of the product (carboxymethylated PW) was 25.00 g.

Figure 2.2

Carboxymethylated CMPW

2.1.2.5 Thermal crosslinking of CMPW

A sample of CMPW (5.00 g) was heated in an oven at 165 ^{o}C for 15.00 min. The The obtained cured sample of CMPW-X was evaluated for water solubility and carboxyl degree of substitution.

2.1.2.6 Carboxyl degree of substitution of CMPW-X

The carboxyl degree of substitution (DS) of CMPW-X was determined using the standard testing method ASTM 2005 [47].

A sample of CMPW-X (3.0 g) was suspended in a 100 mL of 95% ethyl alcohol and mixed for 20 min at room temperature. A 4.0 mL of nitric acid (concentrated) was added to the sample suspended in ethanol. The produced suspension was mixed for 20 min with no heat. The liquid was removed by decantation and the solid was rinsed with 65% ethanol (4 x 50 mL).

Each wash was performed by stirring the solid in the 65% ethanol solution for 20 min, then liquid was removed by decantation. In the last wash methanol was used and the solid was collected by filtration under vacuum and plced under reduced pressure for drying at 65 ^{o}C until it dried, about 2 hrs.

A 1.0 ±0.001 g solid of obtained CMPW-X was placed in an Erlenmeyer flask containing a 100 mL of distilled water and 25.0 mL of NaOH (of 0.3N). The suspension was mixed for 35 min, then titrated with HCI (0.3N) in the presence of two drops the indicator phenolphthalein to the end point. The calculation was performed according to Equations (1) and (2).

A blank was determined by titration of 25.00 ml 0.3 N Sodium hydroxide with 0.3 N HCl using phenolphthalein indicator, in three runs.

2.1.2.7 Water Solubility of CMPW and CMPW-X

A 2.00 g sample of CMPW was placed in 50 mL of distilled water and mixed for 2 h, collected by suction filtration, and dried at 105 ^{o}C for two hours. Theproduced was placed in a desiccator to cool down then weighed. A 0.5 g drop in the mass was noticed. Recovered samples weigh was about 1.5 g A 2.00 g sample of CMPW was placed in 50 mL of distilled water and mixed for 2 h, collected by suction filtration, and dried at 105

^{o}C for two hours. The sample was placed in a desiccator to cool down then weighed. A 0.05 g drop in the mass was noticed.

2.2 Determination of optimal extraction parameters

2.2.1 Cobalt Solutions Preparation

A 4.9 g sample of Cobalt nitrate $Co(NO_3)_2.6H_2O$ was used to prepare a stock solution, The quantity was placed in 1 L volumetric flask and dissolved in 1.00 L of deionized water. From the stock solution 5.00 solutions with various concentrations of 5.00, 10.00, 20.00, 30.00, 40.00 and 50.00 ppm of cobalt ion were prepared.

2.2.2 Calibration Curves

The calibration curves for the standard solutions were prepared by measuring the absorbency (flame atomic absorption spectroscopy (FAAS)) of the five standard solutions of cobalt ion and plotted against concentration as shown in Figures 3.6.

To evaluate the impact of several factors, including initial concentration, time, dosage, pH, and temperature at the effectiveness of hazardous metal removal by CMPW, a calibration curves was generated using diluted solutions. All of the tested solutions adsorption was quantified using FAAS (Flame Atomic Absorption) at a wavelength of 240.7 nm for cobalt. Using the resulting curves, the concentrations of residual cobalt ions in the filtered samples were estimated using the generated calibration curve

2.2.3 Extraction of Co(II) by Batch process

The extraction was done by adding a specific quantity of CMPW-X polymer to the several solutions of cobalt(II) in a 20 mL plastic vials with known concentrations, then the vial was capped and mixed at constant temperature and pH, based on the factor under study, for a known period of time. Using a syringe, a sample of the suspension was collected then filtered by passing the solution through a 0.45 µm filter was used to filter the solution. The filtrate was collected and evaluated for residual Co(II) by atomic absorption spectroscopy AAS.

2.3 Effect of dose CMPW-X on removal of Co(II)

To figure out the optimal amount of carboxymethylated CMPW-X for Cobalt (II) adsorption, different quantities of the carboxymethylated CMPW-X (5.00 mg, 10.00 mg, 20.00 mg, 30.00 mg, 40.00 mg) were added to five plastic bottles containing 10.00 mL with 20.00 ppm metal ion standard solution. The pH of all five solution was set to 6.0 and were mixed for 30.00 minutes at room Temp.. FAAS was used to determine the residual concentrations of Co (II).

Table 2.1

displays the results of the Carboxymethylated CMPW-X dosage effect on the adsorption of cobalt (II) ions

Polymer dose (mg)	[Co(II)] (ppm)	Removal of Co(II)(%)
5.0	0.218	97.82
10.0	0.218	97.82
20.0	0.217	97.83
30.0	0.205	97.95
40.0	0.185	98.15

2.4 Effect of Concentration of Co(II)

To determine the optimal concentration of Co(II) ion solution, the perfect dosage of CMPW-X polymer 40.00 mg for cobalt was added to five plastic bottles, possessing 10.00 mL of various standard Co(II) concentrations (1.00 ppm, 5.00 ppm, 10.00 ppm, 20.00 ppm, and 40.00 ppm) was shaken mechanically under these conditions pH 8, 30.00 min contact time and temperature 25 ºC.

Table 2.2

Effect of Concentration of Co(II)

Concentration (ppm)	[Co(II)] (ppm)	Removal of Co(II)(%)
1.0	0.030	99.4
5.0	0.044	99.5
10.0	0.065	99.6
20.0	0.078	99.7
40.0	0.064	99.8

2.5 Effect of Contact Time

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

Five solutions of cobalt nitrate with optimum concentration (40.0 ppm) were placed in five vials, then the CMPW-X dosage that gave maximum removal efficiency 40.00 mg polymer with cobalt ion, was added to the solution, then shacked mechanically at 8 pH and 25 ºC for various times (20.00, 25.00, 30.00, 40.00, and 50.00) minutes, and at the end of each period, the metal ion concentration of Co(II)filtrate was measured using FAAS and summarized in table 2.3 in Appendix A.

Table 2.3

Effect of Contact Time

Contact time (min)	[Co(II)](ppm)	Removal of Co(II)(%)
20.0	0.006	99.9
25.0	0.156	98.4
30.0	0.131	98.6
40.0	0.001	99.0
50.0	0.600	98.3

2.6 Effect of Temperature

In order to examine how temperature affects the adsorption process, 10.00 mL of Co^{+2} with a 50.00 ppm standard solution and 50.00 mg of the CMPW-X polymer were combined, also 40.00 mg derivatized CMPW-X polymer added to 10.00, 50.00 ppm standard solution at pH of 4.50. Each solution was shaken mechanically in water bath at the varying temperature (15, 20, 25, 30 and 40 ºC) to the optimum time 20.00 min. At the end of each time interval, metal ion concentration of Co(II) in each filtrate was measured using FAAS and summarized in Table 2.4 in Appendix A.

Table 2.4

Effect of Temperature

Temp ºC	[Co(II)] (ppm)	Removal of Co(II)(%)
15.0	0.004	99.96
20.0	0.003	99.97
25.0	0.001	99.99
30.0	0.004	99.95
40.0	0.600	94.00

2.7 Effect Of pH

Adsorption was investigated in numerous solutions ranging from acidic pH of 3.00 to basic mediums pH of 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 .00 minutes, adsorbate concentration 40.00ppm, at temperature of 25.0ºC, and CMPW-X polymer dosage 40.00 mg 50.00 mg for Co(II) 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, 8, 9, and 11.5). FAAS was used to measure the metal ion concentration for both Co(II) and Pb^{2+} in each filtrate, and the values are shown in table 2.5 in Appendix A.

Table 2.5

Effect of pH

pH	[Co(II)](ppm)	Removal of Co(II)(%)
3.0	0.16	98.4
4.5	0.17	98.2
8.0	0.12	98.7
9.0	0.15	98.4
11.5	0.16	98.3

2.8 Adsorption parameters optimization

The ideal parameters of adsorption for the Co(II) ions are presented in table 2.2.

Table 2.2

High efficiency at ideal Parameters for cobalt

Adsorbent	Metal ion	%Adsorption	Parameters Adsorbent dosage (mg), concentration (ppm), contact time (min) and Temperature (°C) and pH
CMPW-X	Co(II)	99.0%	40, 40, 30, 25, 8

2.9 Waste-water Purification

A real sample of sewage sample obtained from one of the Palestinian plants located in the in the Westbank teretorries.

was used in this project. The metal ion types and percentage were determined using ICP-MS (Water Center, An-Najah National University, Nablus)

two 10 mL samples of sewage were placed in 50 mL vials. A 50 mg CMPW-X was added to one vial and the other was used as a reference. The pH of the samples was adjusted to 8.0 (best adsorption pH value). The samples were mixed at room temperature for 40 min to ensure that equilibrium was attained. Filtered (0.45 µm syringe filter and residual metal ions concentration was determined using ICP-MS.

Chapter Three

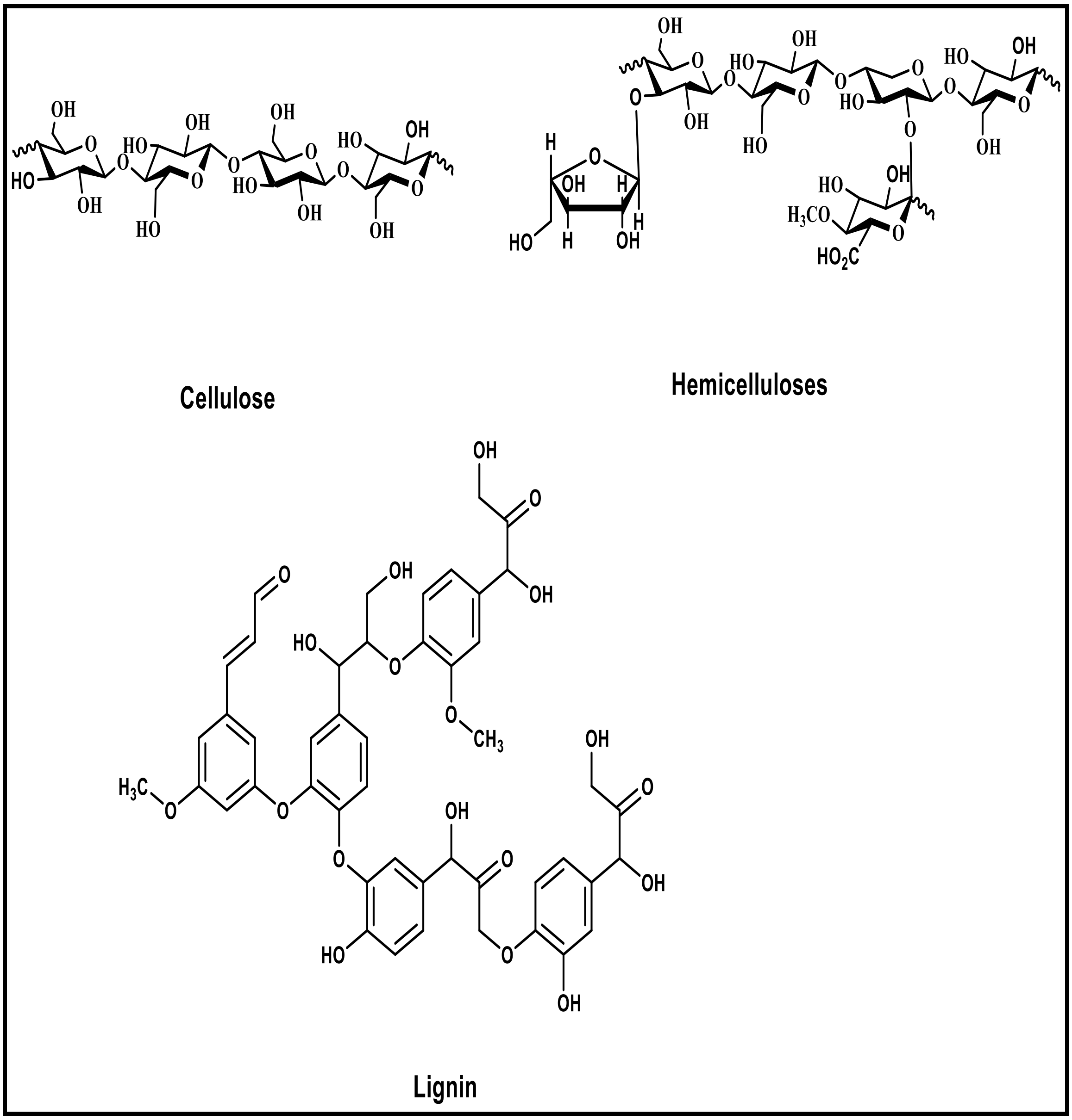
Results and Discussion

3.1 Synthesis of CMPW-X

In this work wastes from palm tree with carboxymethyl functionality was synthesized and converted to composite by thermal curing. The composite was used as an adsorbent for toxic metals present in wastewater. Carboxymethylated palm waste was prepared by reacting a ground sample of the waste with sodium chloroacetate in alkali medium and isopropyl alcohol as a solvent. The reaction was performed after subjecting the palm waste to Soxhlet extraction with ethyl acetate. The palm tree waste is composed of cellulose, lignin, and hemicellulose (Figure 3.1). All three components carry hydroxyl groups which in alkali medium are converted to alkoxide which behave as nucleophile that undergo nucleophilic substitution reaction (S_N2) with sodium chloroacetate and add carboxyl methyl group to cellulose, lignin and hemicelluloses. The present of the carboxyl groups in addition to hydroxyl group and the aromatic ring in the waste components makes it excellent candidate for application is in wastewater purification from toxic metal ions.

Figure 3.1

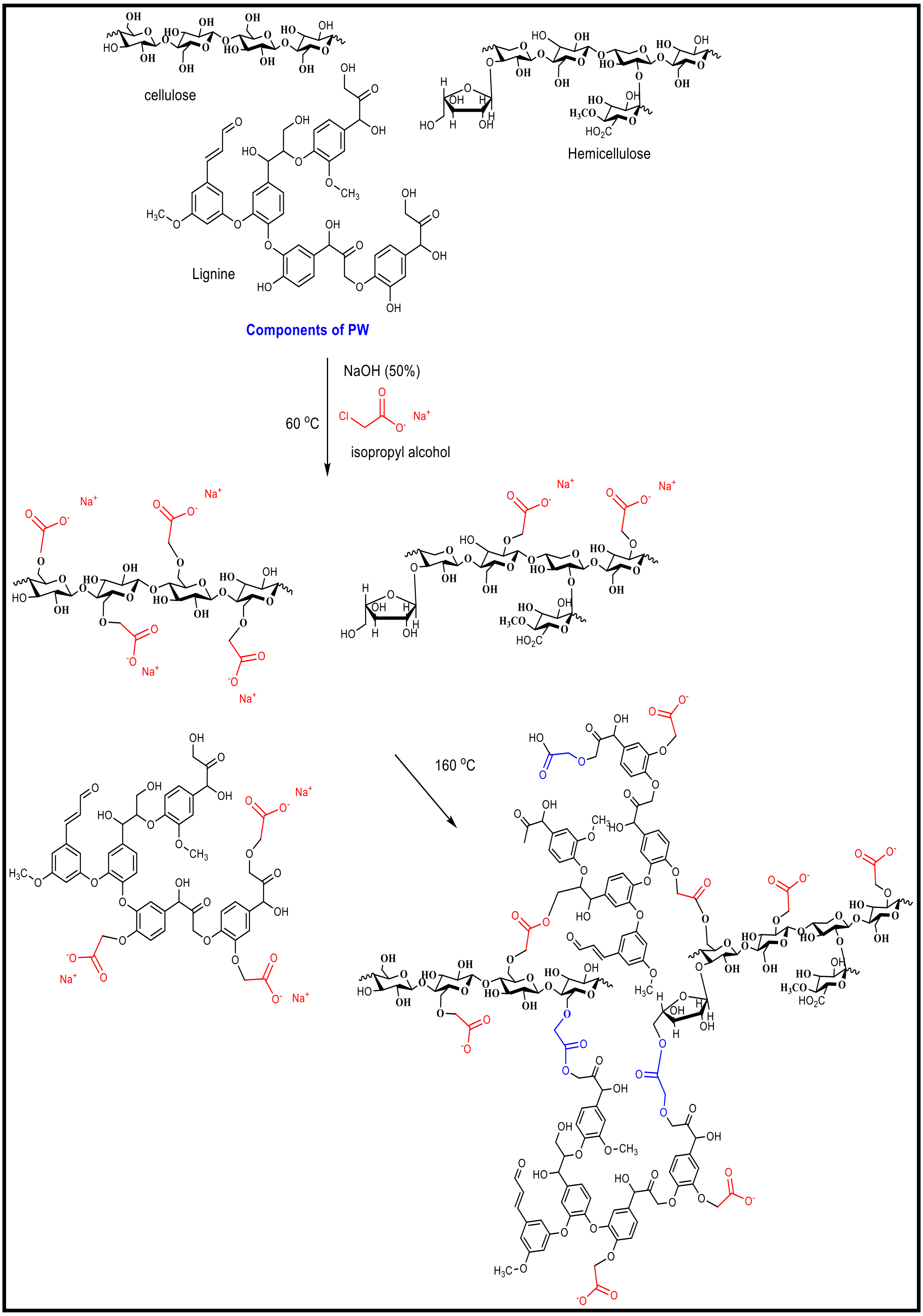
Components and chemical structures of palm tree waste components



The preparation method is summarized in Figures 3.2 and 3.3. Figure 3.2 shows the S_N2 reaction of the alkoxide with sodium chloroacetate and the thermal curing is shown in Figure 3.2.

Figure 3.2

The chemical reaction of adding ionic functionality to PW components and formation of CMPW-X by thermal cursing

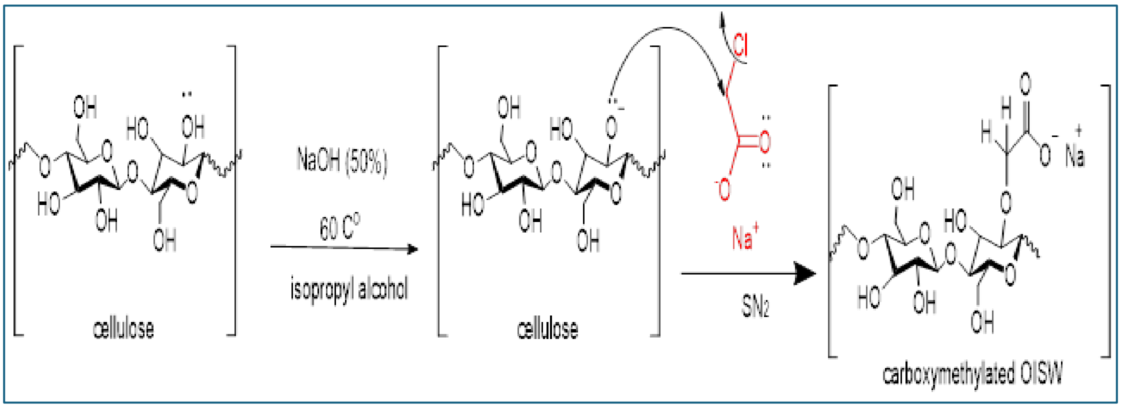


3.1.1 Reaction mechanism

Carboxylation reaction mechanism is shown in Figure 3.4, As mentioned above is a S_N2 reaction. It involves a transition state of displacing the chloride with the alkoxide and formation of an ether linkage.

Figure 3.3

Reaction mechanism of cellulose carboxymethylation



3.1.2 Curing stage

During the curing stage the OH reacts with the carboxyl group to form an ester linkage between the polymer chains. During the curing step, the carboxylate components of the PW (cellulose, lignin, and hemicellulose) are expected to react together by condensation reaction to form a network of a 3D 3structure that is composed of various functional groups that act as a chelating agent for metal ions.

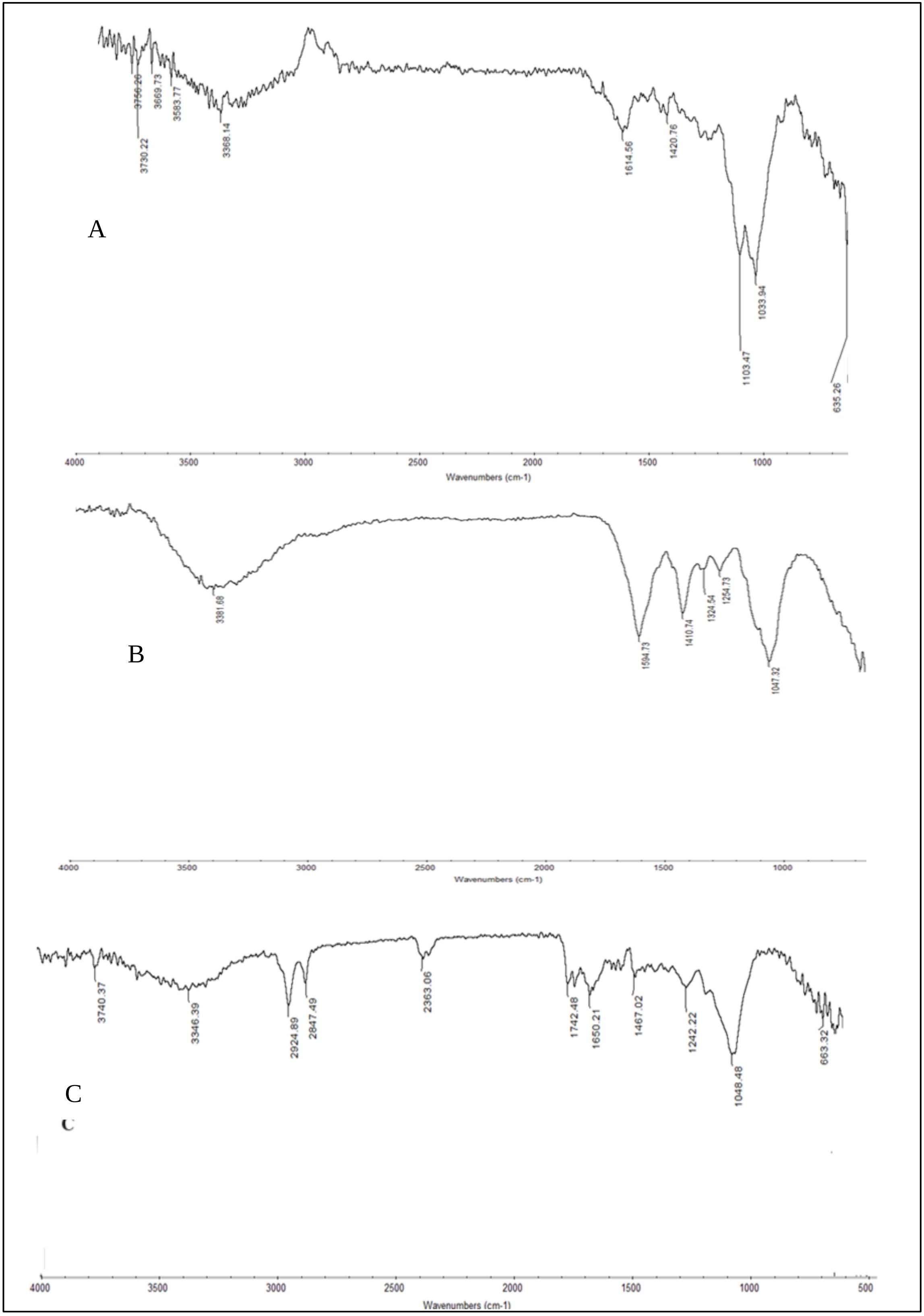
3.2 Polymer Characterization

3.2.1 FT-IR of Palm waste (PW)

The FT- IR spectrum of PW is deicted in figure 3.5A. The obtained spectrum shows peaks that appear in carbohydrate polymers (cellulose and hemicelluloses). The O-H stretching appears at 3670 cm-1. The C-O and O-C-O starching appear at 1100 and 1033 cm-1, respectively.

Figure 3.4

FT-IR spectrum of palm waste



Note: A) FT-IR spectrum of palm industry solid waste, B) FT-IR spectrum of CMPW, C) FT-IR spectrum of CMPO-X

3.2.2 FT-IR of CMPW and CMPW-X

As seen in Figure 3.5B, many peaks appeared in the IR spectrum of CMPW-X, the peak at 3391 corresponding to the O-H stretching, the weak band at 2944 cm^{-1} could be attributed to alkyl C-H stretching. A strong broad band appear at 1564 cm^{-1} corresponding to the C=O of the carboxylate and the peak at 1410 could be attributed to the CH_2 bending. Another strong broad shows at 1049 cm^{-1} could be attributed to the C-O bending. This peak usually appears in the carbohydrate polymers.

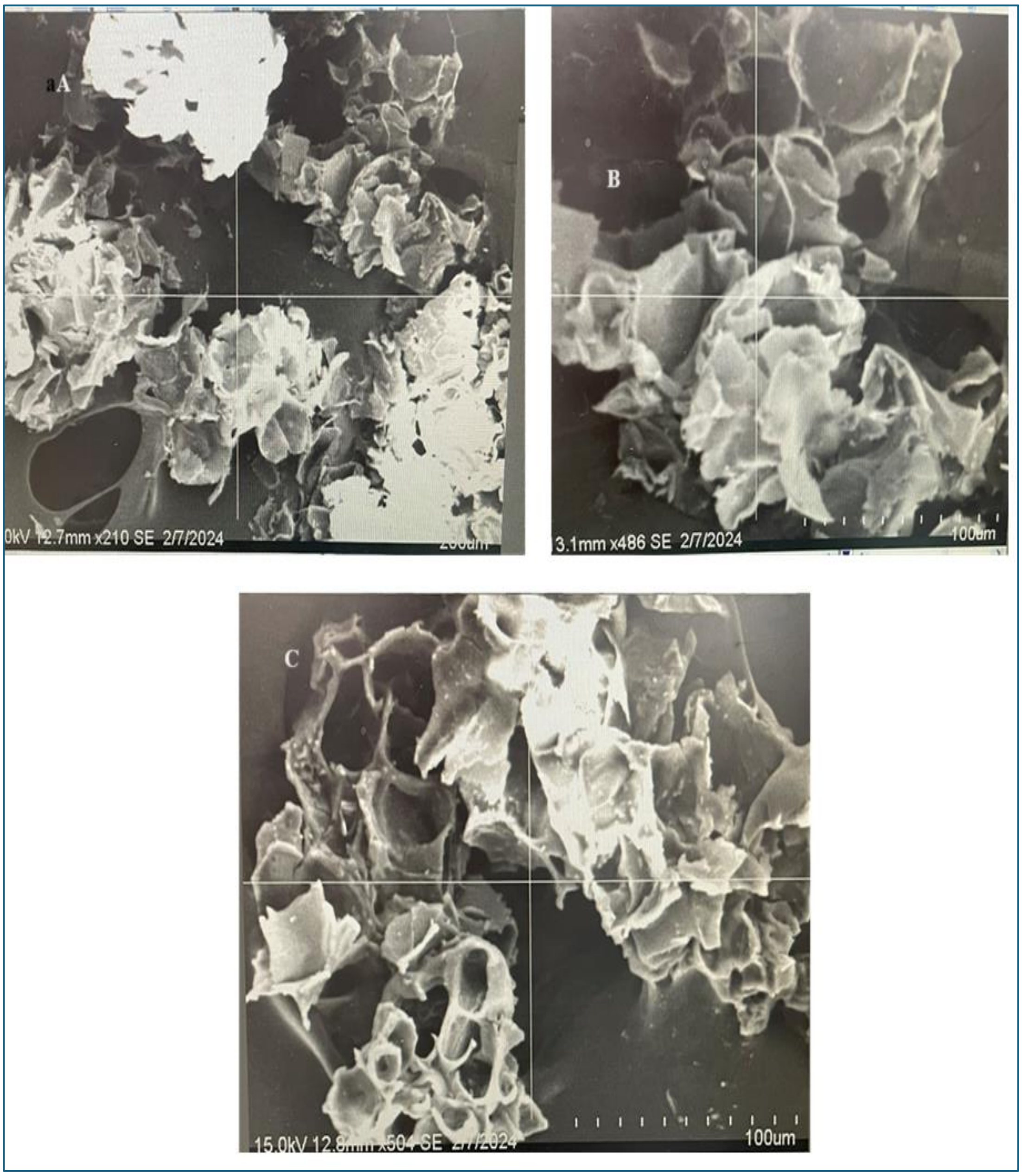
The FT-IR spectrum of CMPW-X is shown in figure From Figure 3.1.C. The peaks appear in the IR spectrum are like those shown in the IR spectrum of CMPW except there is some shift in the wavenumber of some peaks and a new peak appeared at 1740 cm^{-1} which could be related to the carbonyl (C=O) of ester developed during the curing process. The C=O peak shifted to 1650 cm^{-1}. The peak observed at 1325 cm$^{–1}$ can be related alkyl group. The peak at 3390 cm^{-1} is due to the O-H stretching of carboxyl and alcohol. The IR spectrum shows clearly that carboxyl and ester group are present in the final product.

3.2.3 Electronic microscope (SEM)

The surface structure of CMPW-X was studied by SEM, obtained images are shown in Figure 3.6. The images show a fiber structure that is highly porous. These properties make the prepared polymer very useful for metal ions removal from water. High porosity and hollow fiber cause an increase in the polymer area exposed to metal ions. Thus, increases the number of binding sites the efficiency of adsorption.

Figure 3.5

SEM images of CMPW-X at



Note: A) 250x, B) 500 x, C) 100X.

3.2.4 Carboxyl Content of CMPW

In the carboxymethylation of the CMPW carboxyl group was attached to the CMPW-X, the carboxyl content plays a major role on the adsorption efficiency of toxic metal ions. As the carboxyl content increases percent removal of metal ions increases, since it a chelating ligand for metal ions. Due to these reasons, it is crucial to determine quantitatively the DS of carboxyl on CMPW-X, this was carried out by back-titration technique as mentioned in experimental chapter. The carboxymethylated PW (CMPW-X) was suspended in a solution of sodium hydroxide for a certain period then titrated with HCl solution of known concentration. Phenolphthalein was added as an indicator during the titration process. The degree of substitution of -COOH on CMPW-X was calculated as shown in equations 3.1 and 3.2. The degree of substitution (DS) represents the average number of carboxyl groups per repeat unit.

$$Carboxyl\ equip\ in\ CMPW-X = \frac{V\ NaOH\ (ml)\ NNaOH*V\ HCL(ml)NHCL}{Mass\ (g) of\ CMPW-X} \qquad \text{Eq 3.1 [64]}$$

$$DS = 0.162 * Carboxyl \frac{milliequivalents}{(1-0.058*Carboxyl\ milliequivalent)} \qquad \text{Eq 3.2 [65]}$$

From Eqs 3.1 and 3.2 the degree of substitution was determined to be 0.83, about 2 carboxyl group per three anhydroglucose units.

3.3 Cobalt adsorption by CMPW-X

The goal of this work is to convert waste materials of palm tree to novel polymer with high efficiency for metal ions present in wastewater and to use it to remove dangerous materials form sewage water. This goal was achieved by studying the capacity of adsorption of the synthesized CMPW-X towards Co(II) ions.

The residual metal ion concentration was determined by Atomic adsorption spectroscopy after the adsorption process. The percentage of Co(II) removal was determined by using Eq.1 .

$$\%E = \left(\frac{(C_0 - C_e)}{C_0}\right) \times 100\% \qquad Eq. 3.3$$

C_0 (mg/L) and C_e (mg/L): the metal ion concertation (ppm) in solution before and after adsorption procedure, respectively

The Co(II) ions calibration curve (Figure 3.7(appendix)) was generated by determining the absorbency of various diluted solutions of Co(II). The generated calibration curve was used in determining the %residual of Co(II).

3.3.1 Effect of dose on CMPW-X

The results for Co(II) extraction using CMPW-X are presented in Figure 3.7a. The figure shows that as the dosage of CMPW increases, adsorption increased. The highest removal efficiency was attained using 40.00 mg of CMPW-X with a percent removal of 98%. At the initial time the adsorption sites at the surface were empty and available the adsorption rate could fast, then the sites become gradually occupied by cobalt ions..

3.3.2 Effect of initial concentration of metal ion Co(II)

As shown in figure 3.8b, a direct proportional relationship was found between Co(II) concentration and the %removal. The adsorption increased as the Co(II) concentration increased. Co(II) concentration with up to 20 ppm the removal rate reached about 96%. Then it leveled off at 40 ppm of Co(II) with a removal of 99.8%. The 40.0 ppm concentration of Co(II) was selected as the optimum concentration. The results indicate that the adsorption percentage was increased with increasing concentration, since the CMPW-X has high number of binding sites on the surface, that can adsorb Co(II)., then at high concentrations all these sites become equipped.

3.3.3 Effect of absorption time on %removal of Co(II)

The removal of Co(II) by CMPW-X was found to be dependent on time as shown in Figure 3.8c. As the absorption time increases, the %removal was increased. The results indicate two types of mechanisms are involved in the adsorption process binding on the surface-active sites and migration into the interior part of the polymer. The first mechanism occurs instantly while the second mechanism is time dependent. For this reason, as time increases the %removed increases. Then it reached a level where both regions are occupied

3.3.4 Effect of adsorption temperature on %removal of Co(II)

The removal of Co(II) by CMPW-X was found to be dependent on temperature as shown in Figure 3.8d, as the temperature increased the removal rate decreased. The highest %removal was achieved at 25 ^{o}C, with a removal of 99.9%. So, it was taken as the optimum temperature. The results indicate that the prosses of removal of Co(II) by CMPW-X is spontaneous and exothermic. The kinetic energy of adsorbed Co(II) on the increases at temperature higher than room, this caused the adsorption equilibrium to shift back to formation of free metal ion.

3.3.5 Effect of pH on %removal of Co(II)

monitoring the pH value of Co(II) solution is a very important factor in adsorption method, as it impacts the adsorption sites Co(II). The experimental conditions were set at the optimum determined conditions of temperature 25 °C, adsorption time 30 min, 40.00 ppm concentration of Co(II), and CMPW dose of 40.00 mg.

Obtained results are shown in Figure 3.8d, the tested pH values were ranged 3.0 to 11 The obtained results show that Co(II) were eliminated significantly at a pH of 8.0 slightly basic. The percent Removal increased by increasing the pH until a pH of 8.0 then started to decline. At basic pH value, the carboxyl in a carboxylate form ($-COO^-$) with a maximum biding efficiency. At pH of 8.0 the % removal was about 92%.

The polymer CMPW-X showed good efficiency at low pH (about 70%), this could be related to the presence of other binding site and the trapping of metal ions in the interior part of the hollow fiber loaded with OH-groups.

3.3.6 Polymer Recycling

A 40 mg sample of CMPW-X was added to a solution of Co(II) placed in a beaker. The temperature was adjusted to 25 ^oC, pH to 8.0. The mixing was carried out for 30 min then centrifuged and decanted. The supernatant was tested for Co(II) residue and the polymer was recycled by suspending it in water 10 mL and adjusting the pH to 2.0. Then centrifuged and reused.

As we shown in Table 3.1. The adsorption was repeated four times using same samples CMPW-X. The regeneration was done by immersing the polymer in an acidic solution with a pH value of 2.5 to liberate the bonded metal ions. The %removal was 98% at the first time then decreased slightly to 97.8% after using it for the second time at the fourth time it dropped to 97%. The results indicate that the polymer could be used several times with loosing efficiency, which makes it value added materials in wastewater purification.

Table 3.1

Effect of recycling of polymer

Cycle	removing extracting
1	98%
2	97.80%
3	97.60%
4	97%

3.4 Adsorption Isotherm

To assess the adsorption at equilibrium of CMPW-X toward Co(II). Two mathematical isotherm models were tested: Eq. 3.2 known as Freundlich and Eq. 3.6 known as Langmuir .

The Freundlich isotherm is a well-known model used for searching deep in mechanistic of the adsorption method in poly layer heterogeneous method. The Langmuir model is preferred for adsorption on a single layer homogeneous surface,

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \qquad \text{Eq.3.4}$$

Where:

K_f, n is the Freundlich constant (mg/g), exponent which indicates the adsorption capacity, intensity and the degree of non-linearity.

The other was Langmuir isotherm [69][70]

$$\frac{1}{qe} = \frac{1}{Qmax\ KlCe} + \frac{1}{Qmax} \qquad \text{Eq 3.5}$$

Where;

Ce: the concentration of ions in equilibrium (ppm).

Qmax: The adsorbent monolayer adsorption capacity (mg/g).

K_l: The Langmuir affinity constant (L/mg).

At equilibrium, qe is the amount of adsorbed per unit mass of polymer (mg/g).

3.4.1 Langmuir adsorption isotherm

Since all active centers have the same amount of energy, monolayer adsorption and desorption on one active center have no effect on the adsorption on another active center. This is the foundation of the Langmuir model, which is based on the number of homogeneously distributed active regions across the surface of the adsorbent CMPO-X. [66,67,68]

The amount of adsorbed per unit mass of polymer (mg/g) at equilibrium is known as qe.Adsorption follows this paradigm when the 1/qe vs. 1/ce graph plot shows a straight line with a high R2 value.

The isotherms graph indicates by the value of R_L as being irreversible (R_L=0), favorable (0 < R_L< 1), linear (RL=1), or unfavorable (R_L> 1)

Obtained results are summarized in Table 3.2a and plotted in Figure 3.9a

Table 3.2

Langmuir Isotherm

Initial Conc of Co(II) (ppm)	Final Conc of Co(II) (ppm)	Adsorption (%) PPUF	Qe	1/qe	1/ce	ln qe	ln ce
5	0.03	99.4	39.74	0.025	33.3	3.682	3.5
10	0.044	99.5	39.78	0.02513	22.7	3.683	3.1
20	0.065	99.6	39.81	0.0251	15.3	3.684	2.7
30	0.078	99.7	39.84	0.02509	12.8	3.685	2.5
40	0.064	99.8	39.89	0.02506	15.6	3.686	2.7

Table 3.3

Freundlich Isotherm

Conc (ppm)C_f	[Co(II)] (ppm)C_i	q_e	Ln c_e	Ln q_e
0.03	5	39.74	3.50	3.68
0.044	10	39.78	3.12	3.68
0.065	20	39.81	2.73	3.68
0.078	30	39.84	2.55	3.68
0.064	40	39.89	2.74	3.68

The obtained R_L is about 0.877.

3.4.2 Freundlich isotherm model.

An empirical modal suited for adsorption processes occurring over multiple layers and on heterogonous surfaces with different adsorption energies is the Freundlich isotherm.

A straight line with an R2 value close to 1 indicates that the adsorption follows this model when plotting ln (qe) vs. ln (Ce) using Eq. 5, the linearized form of the Freundlich isotherm. Adsorption is also perceived positively if $n > 1$.

The constants Kf and n were found using the slope and intercept of the log (Ce) against log (qe) plots. Table 3.3b provides the parameters of the Freundlich model based on CMC for the sorption of lead by two polymers.

The obtained results are summarized in tables 3.4 and 3.5 and plotted in figure 3.9b

Table 3.4

Parameters for Freundlich adsorption isotherms of carboxymethylated CMPW

Metal ion	Freundlich		
	R^2	N	K_f
Co(II)	0.683	0.004	8.872

The adsorption results indicates that adsorption of Co(II)using CMPW-X polymer obeys Freundlich isotherm.

3.5 Adsorption Kinetic

The adsorption capacity qe (mg/g) was calculated at optimum determined conditions using equation 2.6

$$q_e = (C_i\text{-}C_f/m) * V \qquad \text{Eq. 2.6}$$

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

3.5.1 Pseudo-first order model

$$ln(qe - qt) = ln\, qe - K1t \qquad \text{Eq 3.6}$$

K1: the first-order rate constant (min)

qe: the equilibrium amount of solute absorbed per unit weight of adsorbent (m g/g).

qt: the amount of solute absorbed 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.6b

The calculated values are summarized in table 3.6a, the value of various parameters are shown in Table 3. obtained from the plot shown in Figure 3.11a

Table 3.5

Pseudo-first order model values

Time (min)	Initial Conc Of Co (II)	final Conc Of Co(II)	Percentage of removal (%)	qt	ln (qe-qt)
10	5	0.004	99.96	1.99	1.23
20	10	0.003	99.97	3.99	0.35
25	20	0.001	99.99	7.99	2.08
40	30	0.001	99.95	11.99	2.48
50	40	0.005	99.94	15.99	2.64

Table 3.6

pseudo-first order model for the adsorption of Co(II)on CMPW-X

Metal ion	Adsorption kinetic pseudo-first order model			
	R^2	Theo. q_e	Exp. q_e	K_1
Co^{2+}	0.98	39.8	7.9	2.7

3.5.2 Pseudo-second order model

$$\frac{t}{qt} = \frac{1}{k2q^2e} + \frac{t}{qe} \qquad \text{Eq 3.7}$$

K2: the second-order rate constant (g mg min')

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

qt: the amount of solute absorbed 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.

From correlation coefficients (R^2) values of pseudo-first and second order the adsorption of Co(II) on CMPW-X, it seems to obey pseudo-first order since ($R^2 = 0.98$).

3.5.3 Adsorption Thermodynamic

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 CMPW-X.

Table 3.9

Thermodynamic value for Vant Hoff plots for adsorption of Co(II) by CMPW-X

Temp C°	[Co(II)] (ppm)	1/T (K^{-1})	ln kd qe=39.8944
10.0	5.0	0.002681	3.2
20.0	10.0	0.002545	2.8
25.0	20.0	0.002513	2.5
30.0	30.0	0.002481	2.4
40.0	40.0	0.002421	2.3

Table 3.10a Shows that the adsorption of cobalt metal ion on CMPW-X 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 25 °C.

3.6 Conclusion

In this work, CMPW-X was purified by Soxhlet extraction method, and derivatized with the ionic functional groups CH_2COOH by reacting it with sodium chloroacetate in ana alkaline medium. The derivatized CMPW was thermally cured to reduce water solubility and eliminate extractives. In addition to develop a 3D structure that is highly stable and effective in metal removal. The cured CMPW-X was characterized by IR and SEM. The produced CMPW-X showed excellent efficiency toward Co(II) with a quantitative removal. It also showed excellent efficiency toward all metal ions present ina real sample of wastewater. The kinetic study showed that the adsorption process follows first order kinetic and obeys Freundlich isotherm model in which the adsorption occurs on various sites at various quantities. Thermodynamic analysis showed that the adsorption is spontaneous and exothermic as the ΔG value is negative. The ideal esteem of the determined value of the parameters for Co(II) removal were 40.00 mg does, 40.00 ppm initial concentration, pH of 8, temperature 25 ^{o}C, and a contact time of 30.00 min.

3.7 Recommendations

- Utilizing nanoscale technology of CMPW-X.
- Producing CMPW on large scale quantity and run a real trail at one of the Palestinian plants.

List of Abbreviations

Abbreviations	Meaning
CM	Carboxymethyl
CMPW-X	Carboxy methylated palm waste cross-link
FAAs	Flame Atomic Absorption Spectrometer
ICP-MMS	Inductively Coupled Plasma Mass Spectrometer
SEM	Scanning electron microscope analysis
R^2	Correlation coefficient (regression coefficient, fitting coefficient)
C_f	Concentration of metal ions at equilibrium(mg/L)
C_i	Initial concentration of metal ions (mg/L)
Qe	The mass of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g)
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
K_d	The thermodynamic gas constant
R_L	Dimensionless constant separation factor
1/n	Dimensionless Freundlich constant indicates how favorable the adsorption process is.
$\Delta H°$	The change in enthalpy
K_{id}	The Intraparticle Diffusion Rate Constant
$\Delta S°$	The change in entropy
$\Delta G°$	The change in Gibbs free energy
R	The universal gas constant
T	The Absolut temperature

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Appendices

Appendix A

Tables

Table A.1

Contact Time Effect on The Adsorption of Cobalt (II) on the Carboxymethylated CMPW

Contact time (min)	[Co(II)](ppm)	Removal of Co(II)(%)
20	0.006	99.9
25	0.15	98.4
30	0.13	98.6
40	89	99
50	0.6	98.3

Table A.2

Temperature Effect on the adsorption for Co^{2+} ion on Carboxymethylated CMPW

Temp ^{o}C	[Co(II)] (ppm)	Removal of Co(II)(%)
15	0.004	99.96
20	0.003	99.97
25	0.001	99.99
30	0.004	99.95
40	0.6	94

Table A.3

Ph Value Effect on the Adsorption of Co(II) Ion on the CMPW-X

pH	[Co(II)](ppm)	Removal of Co(II)(%)
3	0.16	98.4
4.5	0.17	98.2
8	0.12	98.7
9	0.15	98.4
11.5	0.16	98.3

Table A.4

Recycle Effect on the Adsorption of Co(II) Ion on the CMPW-X

cycle	removing extracting
1	98%
2	97.80%
3	97.60%
4	97%

Table A.6

ICP results

Metal Ions	Initial Concentration(ppm)	Adsorption Efficiency of CMOISW	
		Final Concentration	%Removal
Ag	25	0.01	99.95%
Al	12515	36.2	99.71%
As	10480	15.9	99.85%
B	237352	196.8	99.92%
Ba	12896	43.0	99.67%
Be	13	0.02	99.78%
Bi	64	0.12	99.80%
Car	17738337	44379.7	99.75%
Cd	398	0.01	100.00%
Co	11434553	156.1	100.00%
Cr	46346	79.1	99.83%
Cu	2150	8.19	99.62%
Fe	22500	135.7	99.40%
Ga	289	0.7	99.74%
Li	2367	4.5	99.81%
Mg	18572994	40599.1	99.78%
Mn	17237	1.14	99.99%
Mo	901	1.83	99.80%

Ni	30734	7.90	99.97%
Pb	89	0.26	99.70%
Rb	14366	26.5	99.82%
Se	1488	0.8	99.94%
Sr	148754	353.1	99.76%
Te	58	0.19	99.66%
Ti	1	0.005	99.50%
U	82	0.11	99.85%
V	22341	36.3	99.84%
Zn	23599	17.05	99.93%

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Table 3.1

Effect of recycling of polymer

Cycle	removing extracting
1	98%
2	97.80%
3	97.60%

Table 3.2

Langmuir Isotherm

Initial Conc of Co(II) (ppm)	Final Conc of Co(II) (ppm)	Adsorption (%) PPUF	Qe	1/qe	1/ce	ln qe	ln ce
5	0.03	99.4	39.74	0.025	33.3	3.682	3.5
10	0.044	99.5	39.78	0.02513	22.7	3.683	3.1
20	0.065	99.6	39.81	0.0251	15.3	3.684	2.7
30	0.078	99.7	39.84	0.02509	12.8	3.685	2.5
40	0.064	99.8	39.89	0.02506	15.6	3.686	2.7

Table 3.3

Freundlich Isotherm

Conc (ppm)C_f	[Co(II)] (ppm)C_i	q_e	Ln c_e	Ln q_e
0.03	5	39.74	3.50	3.68
0.044	10	39.78	3.12	3.68
0.065	20	39.81	2.73	3.68
0.078	30	39.84	2.55	3.68
0.064	40	39.89	2.74	3.68

Table 3.4

Parameters for Freundlich adsorption isotherms of carboxymethylated CMPW

Metal ion	Freundlich		
	R^2	N	K_f
Co(II)	0.683	0.004	8.872

Table 3.5

Pseudo-first order model values

Time (min)	Initial Conc Of Co (II)	final Conc Of Co(II)	Percentage of removal (%)	qt	ln (qe-qt)
10	5	0.004	99.96	1.99	1.23
20	10	0.003	99.97	3.99	0.35
25	20	0.001	99.99	7.99	2.08
40	30	0.001	99.95	11.99	2.48
50	40	0.005	99.94	15.99	2.64

Table 3.6

pseudo-first order model for the adsorption of Co(II)on CMPW-X

Metal ion	Adsorption kinetic pseudo-first order model			
	R^2	Theo. q_e	Exp. q_e	K_1
Co^{2+}	0.98	39.8	7.9	2.7

Table 3.7

The parameters of Pseudo-first order model values

Time (min)	Cf	Qt	t/qt
10.0	5.0	1.9	5.0
20.0	10.0	3.9	5.0
25.0	20.0	7.9	3.1
40.0	30.0	11.9	3.3
50.0	40.0	15.9	3.1

Table 3.8

Adsorption kinetic parameters (pseudo-second order model) for the adsorption of Co2+ on CMPW-X

Adsorption kinetic pseudo-second order model			
K_2	Exp. q_e	Theo. q_e	R^2
210.12	7.99	39.89	0.62

Table 3.9

Thermodynamic value for Vant Hoff plots for adsorption of Co(II) by CMPW-X

Temp C°	[Co(II)] (ppm)	1/T (K^{-1})	ln kd qe=39.8944
10.0	5.0	0.002681	3.2
20.0	10.0	0.002545	2.8
25.0	20.0	0.002513	2.5
30.0	30.0	0.002481	2.4
40.0	40.0	0.002421	2.3

Table 3.10

Adsorption of Co(II) by CMPW-X, Values of thermodynamic parameters

Metal ion	Temp.(K)	Adsorption Thermodynamics		
		ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol.K)
Co(II)	283	4601.05	7.21674E-06	0.00032
	293	6229.14		
	298	5896.39		
	303	4805.39		
	313	3707.17		

Appendix B

Figures

Figure 3.7

Cobalt Calibration Curve

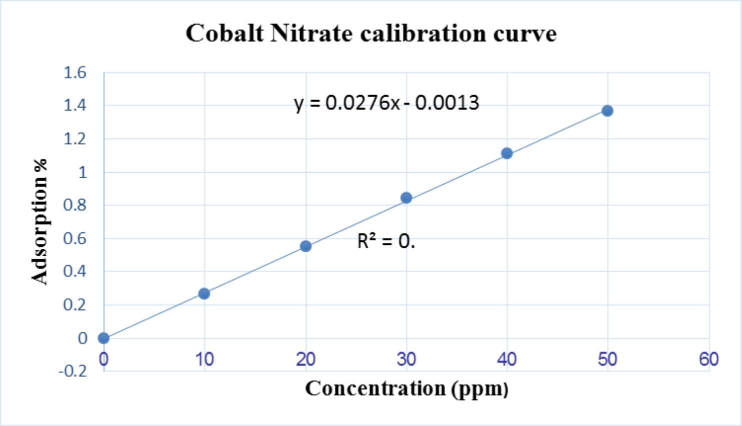


Figure 3.6

Effect of Dosage, Co(II) initial concentration, time, temperature and pH on %removal of Co(II) by CMPA-X

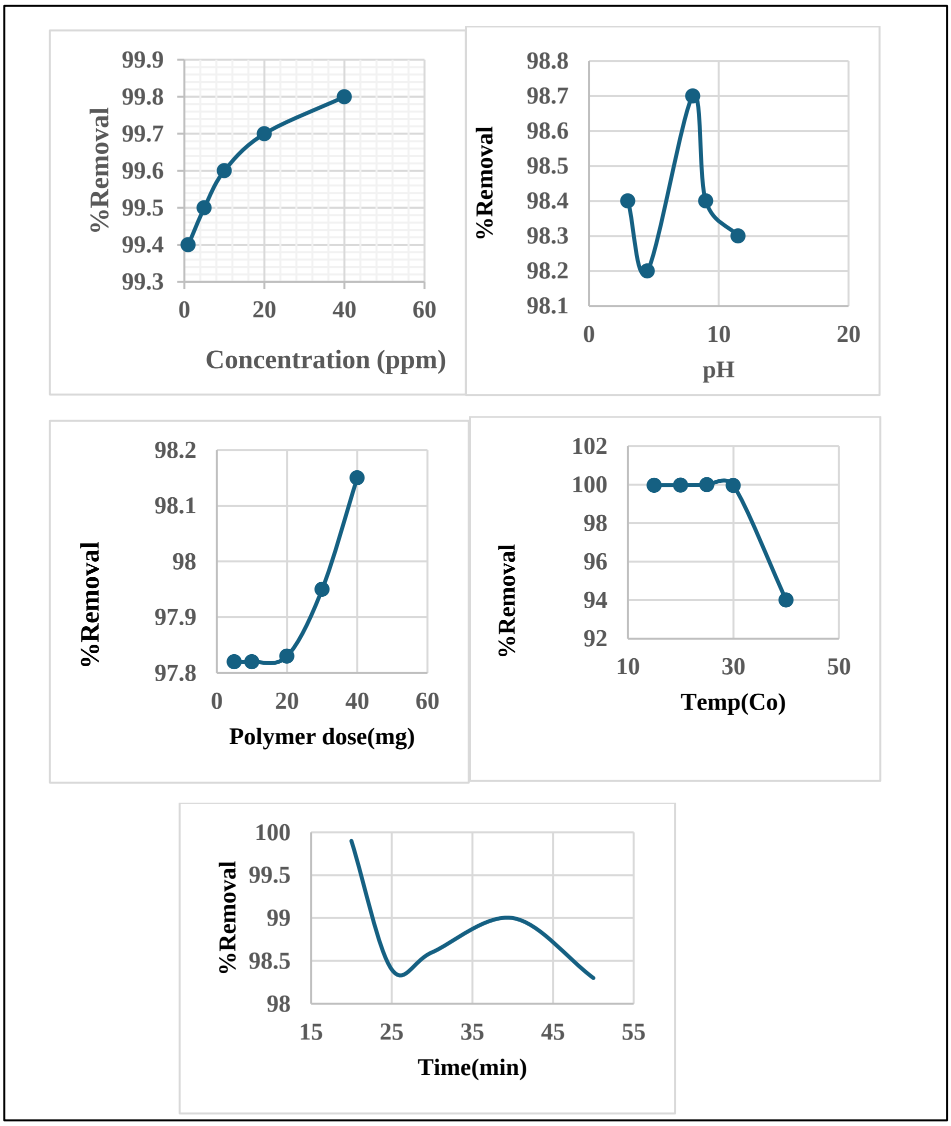
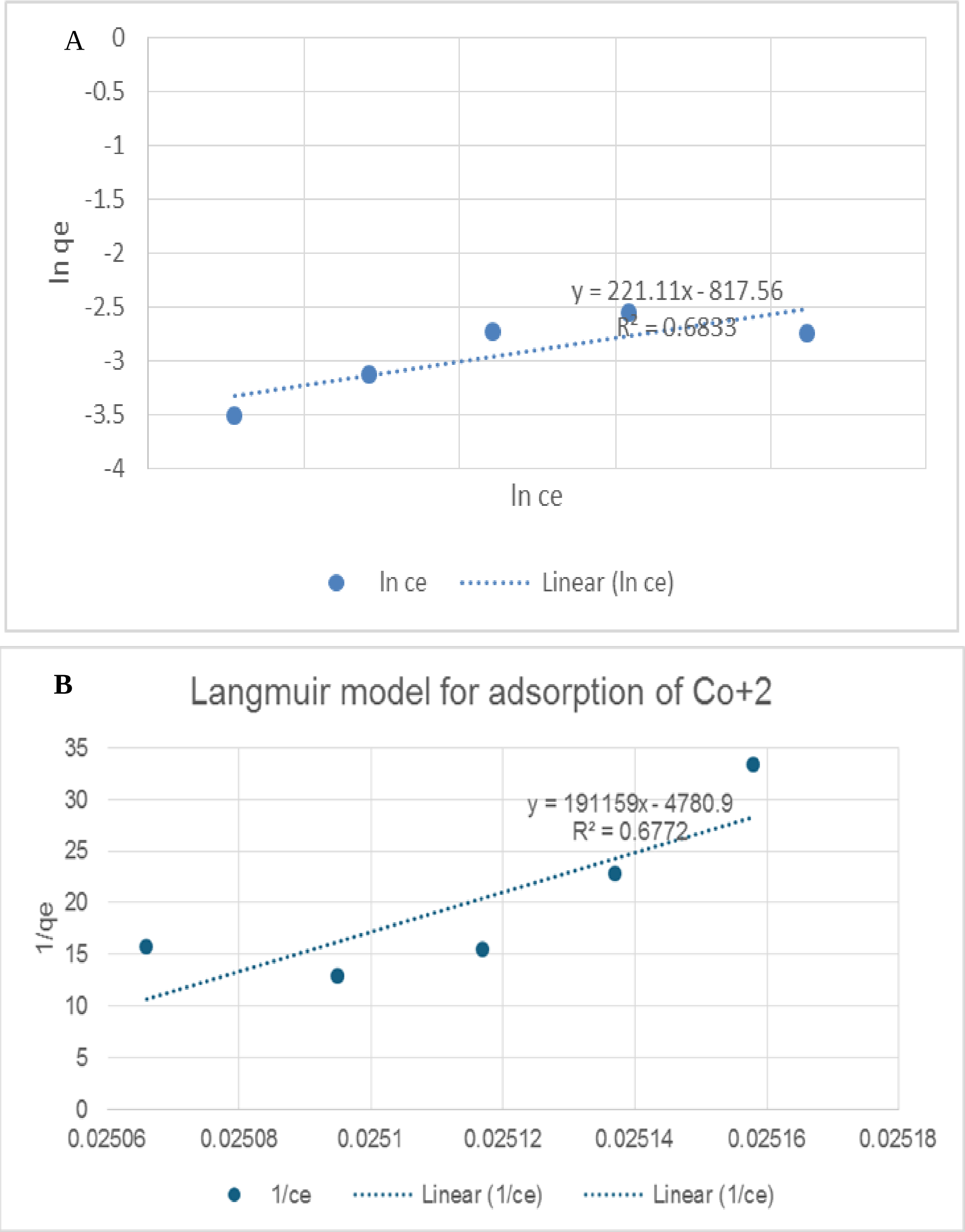


Figure 3.9

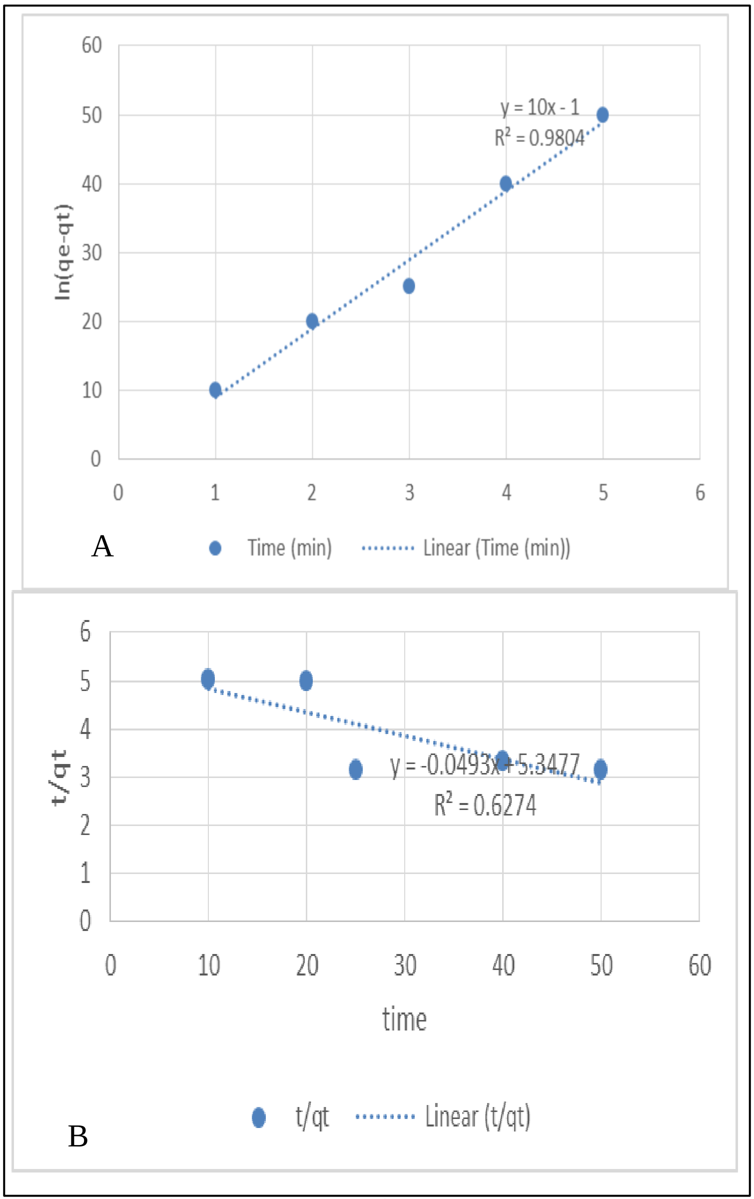
Adsorption of Co(II) on CMPW-X



Note: A) Langmuir model B) Freundlich model

Figure 3.11

Adsorption kinetic



Note: A) Pseudo-first order model for the adsorption of Co(II), on CMPW-X, B) Adsorption of Co(II)on CMPW-X Pseudo-second order model

جامعة النجاح الوطنية

كلية الدراسات العليا

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

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الملخص

يعتبر تلوث المياه من أكثر المشاكل العالمية انتشارا والتي يجب النظر إليها بجدية، حيث أن وجود هذه الملوثات في المياه يسبب العديد من الأمراض ويتسبب في الوفاة، حيث يوجد 14000 حالة وفاة يوميا في العالم نتيجة لتلوث المياه. وتعتبر الأنشطة البشرية مثل الصناعات والأسمدة والمبيدات الزراعية والتعدين السبب الرئيسي لتلوث المياه، كما أنها هي المسؤولة بشكل رئيسي عن إطلاق العديد من المواد الكيميائية السامة. بالإضافة إلى ذلك، هناك مصادر طبيعية لتلوث المياه، مثل انطلاقها من الصخور الى المياه الجوفية. يتم تصنيف الملوثات الكيميائية إلى ثلاث فئات: الملوثات العضوية، مثل الهيدروكربونات والمواد غير العضوية، مثل المعادن الثقيلة؛ والمشعة مثل اليورانيوم والرادون. استخدم العلماء العديد من الطرق للتخلص من الملوثات الموجودة في المياه ومن بين هذه الطرق الممتزات وكان التركيز على استخدام ممتزات قائمة على البوليمرات في تنقية المياه من الملوثات حيث يمكن تحسين هذه البوليمرات لجعلها أكثر كفاءة واقل تكلفة في تنقية المياه من الملوثات الخطرة.

تم تشخيص العينة باستخدام FT-IR، وICP، وGC/MS، وFAAS، لفحص بنية العينة، وكشف وقياس الملوثات التي قد تكون ضارة، وتحليل العناصر في المحلول على التوالي. تم تقييم تركيز أيون المعدن، ودرجة الحرارة، ودرجة الحموضة، ووقت اتصال جرعة الممتز وسرعة الاهتزاز كمعلمات تؤثر على عملية الامتزاز. تم فحص فعالية الامتزاز كدالة للتركيز الأولي لأيون المعدن، ومستوى الرقم الهيدروجيني، ووقت

التلامس، وجرعة المادة المازة، ودرجة الحرارة. أعلى امتزاز للكوبالت بلغ $PH = 8$، تركيز $Co = 40$ جزء في المليون، جرعة الممتز = 40 ملجم، زمن التلامس = 30 دقيقة ودرجة الحرارة = 25°م، على التوالي وجميع إجراءات الامتزاز تتوافق مع نموذج حركية الامتزاز من الدرجة الثانية.

الماء أمر بالغ الأهمية للحياة على كوكب الأرض. يمكن أن تؤدي المواد الكيميائية غير العضوية والعضوية المفرطة المستخدمة في قطاعات مختلفة مثل الزراعة أو الصناعة أو المنزل أو غيرها إلى تفاقم الوضع فيما يتعلق بالملوثات في مياه الصرف الصحي. تعتبر الأدوية والدهانات والمواد الكيميائية المنزلية والكائنات الحية الدقيقة ومنتجات العناية الشخصية والمواد الكيميائية للسباكة وغيرها من ملوثات النفايات شائعة في مياه الصرف الصحي. وتعد أيونات المعادن الثقيلة من أكثر هذه الملوثات ضررا لأنها غير قابلة للتحلل ولها آثار طويلة الأمد، بالإضافة إلى أن المعادن عالية السمية .

كلمات مفتاحية: الكوبالت، المعادن الثقيلة، السليلوز كربوكسي ميثيل، كحول الأيزوبروبيل، مخلفات النخيل.