An-Najah National University

Faculty of Graduate Studies

NANOCRYSTALLINE CELLULOSE MELAMINE SCHIFF BASE : SYNTHESIS AND APPLICATION FOR LEAD(II) IONS ADSORPTION

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Dedication

In the beginning, thanks to Allah, who, without His grace on me, would not have completed this thesis and finished my master's journey. Then I dedicate this thesis to my dear father, whom I am always proud of, and to my mother, who was the source of my inspiration and strength and to my life partner who encouraged me to complete this stage and to my family who always been with me.

Thanks are due to my professors who supervised this work and to every teacher who had an imprint in my scientific life.

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All my thanks and love to my family, whom I am proud of, and I dedicate them this success and excellence.

Declaration

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

NANOCRYSTALLINE CELLULOSE MELAMINE SCHIFF BASE : SYNTHESIS AND APPLICATION FOR LEAD(II) IONS ADSORPTION

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: جمانة جلال عبد الكريم ياسين

Signature:

Date: 25-5-2022

List of Contents

List of Tables

List of Figures

List of Schemes

Scheme 3.3: Conversion of cellulose dialdehyde to NCC-Mel 37

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Abstract

Background: In recent years, the need for clean aquatic to cover fast growing human need for food and other activities has increased. An alternative source of water could be wastewater, for this reason wastewater has recently received a lot of attention from researchers all around the world. Serval recent studies were directed toward developing new methods toward wastewater purification, taking into consideration that these methods should be nontoxic, affordable and with high number of turnovers.
In this study, modified cellulose was selected as a metal absorbent that can be used in the purification of wastewater polluted with heavy toxic metals.

Methodology: The modified cellulose was prepared in a multistep process that involves hydrolyzing cellulose isolated from the olive industry solid waste (OISW) to nano-crystalline cellulose (NCC), then oxidize the nano-crystalline cellulose to dialdehyde using sodium periodate ($NaIO_4$), and in the last step, the cellulose dialdehyde was functionalized with melamine as a metal chelating agent.

Nan-ocrystalline cellulose melamine Schiff base was analyzed (NCC-Mel) by FT-IR. The efficiency of prepared cellulose-based Schiff base (NCC-Mel) as an adsorbent for lead (II) ions present in wastewater was evaluated. The effect of various variables such as solution pH, adsorbent dose, solution temperature, time and initial ion concentration were evaluated and optimized.

Results: The efficacy towards removal lead (II) was the highest shown at an initial concentration of lead ion of about 5.0 ppm, 75 mg of adsorbent, at 25 °C, and a pH value of 7 at a mixing time of ten minutes.

Kinetic and thermodynamics obtained data showed that the adsorption of lead (II) ions using the cellulose-based Schiff base polymer (NCC-Mel) follows the second-order kinetics. The calculated q_e (calc.) is approximately equal to that obtained experimentally q_e.

Conclusion: The results indicates that the metal polymer coordination could be the slow step in the water cleaning process. The thermodynamic data showed that the ion removal process is spontaneous and exothermic. The obtained results demonstrate that this studied polymer can be classified as an adsorbent material with high efficiency for toxic metal ions.

Keywords: Adsorption, Cellulose, heavy metals, Lead, Nanocrystlline cellulose melamine, Polymer, Water pollution, Water purification,

Chapter One

Introduction

Water is one of the basic needs and is required by all life on earth, it covers about 71% of the Earth's area. Water is an important factor in the global economy, as many industries depend on water mainly. Moreover, the agricultural sector cannot do without water. The huge development is the use of water in the production of power, which is the basis for the development of the world.

For human health, prosperity, and well-being, there must be enough water. Water must be consumed in appropriate amounts each day to replace bodily fluids and support physiological functions. Furthermore, water is necessary for several productive and recreational activities, as well as for personal and household hygiene. Households with easy access to water sources and higher domestic water use are much healthier than those with more difficult to access water sources and lower domestic water use.

Fresh water is a renewable resource that is reproduced through the natural hydrological cycle, but the unregulated distribution of water all over the world and the increase in number of people and the industrial and agricultural activities have led to pressure on the availability and the quality of this resource.

Insufficient water for humans may lead to problems related to dehydration, which can cause death in severe cases. Several diseases such as Diarrhoeal diseases, infectious hepatitis, Pneumonia, Malari , Kidney disease can also happen.

As the water quantity, water availability and human health are deeply connected it is necessary to maintain the continuity and cleanliness of this resource to meet the needs of the population [1].

Despite the high demand for water and the problem of water pollution has made researchers seek to develop effective ways through which wastewater can be recycled and reused to cover the needs of the population and compensate for the shortage caused by water pollution [1].

1.1 Water pollution

One of the most fundamental humanitarian objectives is to have consistent access to clean, inexpensive water, which is a huge global challenge for the twenty-first century. Suitable materials with high separation capacity, cheap, porosity, and reusability are essential for water purification.

Since the turn of the 20th century, the chemical and pharmaceutical industries have produced a wide range of items that are harmful to the environment and public health, including medicines, antiseptics, , household cleaners, emulsifier, pesticides, dyes, paints, additives, food additives, and personal care items.

A rising number of people are now aware of how these toxins affect groundwater, rivers, and lakes. As a result, it is important to eliminate new contaminants in order to produce safe drink water and solve the problem of water pollution which results from these products.

Water pollution is one of the problems that receive a great attention in the world. The causes of this problem are mostly related to human activities such as drain water, pesticides and fertilizer food and pharmaceutical and other factories. These activities introduce heavy toxic transition metals ions such as Zn, Pb, Hg, Cr, Cd, Cu, As, and Ni into water and make it not useful for human use [2]. These heavy metals are very hazardous and toxic, even at concentration as low as parts per billion (ppb) and tend to cause major causes diseases such as cardiovascular diseases, developmental anomalies, diabetes, neurobehavioral and disorders, and cancer. Therefore, an effective adsorbent method can be applied to eliminate these ions from water and makes usable [3].

Different techniques were developed for metal removal. These include adsorption, coagulation, chemical, flocculation, ion exchange, precipitation, and membrane filtration.

1.2 Heavy metals

Metallic substances with a relative high density compared to water are referred to as heavy metals. Assuming that weight and toxicity are connected, heavy metals also include metalloids like arsenic that can cause toxicity at low exposure levels [3]

Toxic heavy metals (Pd, Pt, Cd, Cu, Pb, Ag, Co, Ni, Hg and Zn) are formed in nature as a result of weather and other factors tend to access in addition to human practices through various industries such as paints, batteries, and the use of fertilizers and pesticides in agriculture [4].

They could reach the human body via the food chain, where they are responsible for bio magnification of the organs accountable for removing toxins from the human organs like kidneys and liver. The metal toxicities depend on several factors such as the route of exposure, dose, and chemical species, as well as the gender, age, genetics, and nutritional status of individuals [5].

In this research we recognize lead (Pb) is a highly toxic heavy metal present in the industrial waste stream and threatens life on earth, and was selected as a model metal in this work.

1.2.1 Lead

Lead is an ancient metal that can be detected in virtually all phases of the inert environment and in all biological systems, and it has numerous industrial applications. For centuries, lead has been mined and used in industry and household products. It is used in the manufacturing of batteries, ammunition, metal products such as solder and pipes, and X-ray shielding devices.

Lead's unique properties of softness, malleability, low melting point, and corrosion resistance make it one of the most widely used metals.

Lead metal is a highly toxic metal ion that targets all human organs. The nervous system is generally the most affected target part of human. The most effective tool to detect high levels of body lead is to measure the concertation of lead in blood samples. Toxication due to lead occurs mainly by consuming food and water contaminated with lead [6].

Lead is known to be quickly enter the blood stream and as mentioned above has sever adverse effects on organ systems like the cardiovascular system, the central nervous system, kidneys, and the body immunity. Therefore, it is necessary to check the concentration of lead in wastewater before it is discharged to surface water and lower its presence to the lower limit that is announced by the World Health Organization (WHO), and that is for lead (II) ions in fresh water about 0.05 ppm [7].

1.3 The methods of water purification

Various technologies and methods have been developed for the removal of pollutants from water include chemical, physical and biological methods. chemical methods such as coagulation, oxidation, precipitation, flocculation and ion exchange. Adsorption, distillation and membrane filtration are an examples of physical methods .in the biological field the bioaugmentation ,anaerobic process and extended aeration have been showed different efficiencies for water purification [8].

Each of these technologies has its own disadvantages, some of the disadvantages include the lack of efficiency in removing impurities, the high cost, in addition to generating toxic side products, as well as adding sever toxic chemicals to the environment. Therefore, an attractive method could be the one that achieve the required efficiency in the purification process at the lowest costs and technical requirements and without producing toxic by-products [8].

Among all methods adsorption is one of the most effective methods and can be run at relatively low cost.

1.3.1 Adsorption

Adsorption is a method of accumulation of solid, liquid or gas solutes on the surface of an adsorbent. The surface on which the adsorbate bonded to is known as adsorbent, and the material absorbed on the polymer surface of the adsorbent is known as adsorbate. The adsorption is classified into chemical and physical adsorption, that depends on the of attraction between adsorbate and the adsorbent [9].

In the process of water purification there are a large number of known solid adsorbents such as agricultural wastes, natural adsorbents, biomass, industrial wastes, metal, carbon and metal oxide spinel ferritebased nanomaterials, dendritic polymers, and nanocomposites. These adsorbents are attractive since they are environmentally friendly, biodegradable, and available at low costs [10].

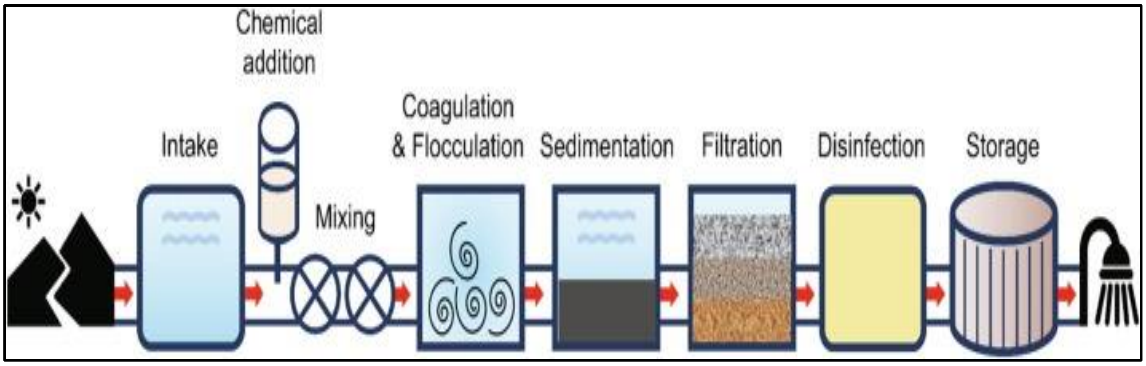
The adsorption process depends on some factors such as surface area, pH, temperature, concentration of adsorbate, adsorbent dose and time.

The most important factor is the surface area of adsorbent, the adsorption efficiency is directly proportional with the surface area of adsorbent [11].

Scheme 1.1 shows a flow process of wastewater plant treatment, the stages include removal of colloidal of inorganic particles by coagulants addition of clay neutralizes the negatively charged particles causing the particles to precipitate. The gravity sedimentation causes the settling of solids, and flotation of debris [12].

Scheme 1.1

a diagram shows a water purification process.



1.3.2 Classification of adsorbents

Adsorbents based on naturally occurring support materials are currently receiving more attention. There are several advantages to using natural support materials, including their availability in huge quantities, inexpensive, and their ability of chemical modification in order to improve their adsorption efficiency. There are several natural materials used as adsorbents for example :chitosan , clays and cellulose.

Industrial wastes, on the other hand, such as fly ash, blast furnace slag and sludge, black liquor lignin, red mud, and waste slurry, are currently being investigated as potential adsorbents for the removal of emerging contaminants from wastewater [11].

According to the sort of the interactions between the adsorbent structure and the adsorptive medium, adsorption process is classified to decomposition (physisorption) and chemical adsorption (chemisorption).

Physisorption is considered a reversible process and rapid, which is mainly composed of van der Waals forces, dipole-dipole forces, and dispersion forces, which is mainly below 50.0 kJ/mol. The change in the electronic states of the adsorbent and adsorbate are menimal. The adsorption forces include London Forces, dipole-dipole attractions, and hydrogen bonding.

An example of physisorption is the adsorption of some gases such as hydrogen on the surface of charcol at low tempreture which can affected by the surface area.

Chemisorption, on the other hand, refers to a chemical bond between the adsorbent and the adsorbate. As a result, the interaction forces are significantly greater, ranging from 60 to 450 kJ/mol, this makes physical adsorption stronger [13]. Due to sensitivity, the chemical identity and the surface structural characteristics can have a significant impact on the type of chemisorption. In chemisorption, the adsorbent and adsorbate are bonded by an ionic or covalent bond.

An example of chemisorptions is Heterogeneous catalysis, in which molecules interact with one another by process of chemisorbed intermediates. The product desorbs from the surface once the chemisorbed species interact.

Both physiosorption and chemisorption depend on various adsorption parameters such as pH, agitation speed, particle sizes, contact time, initial concentration, cationic exchange capacity (CEC) and temperature.

The other important characteristics of a high efficiency adsorbent are the high thermal stability, low pore diameters, and the high abrasion resistance which results in higher surface area of adsorption and hence high percentage of metal removal. Adsorbent material also must be stable at STP conditions to confirm long lasting and reliable use [14].

In the field of water purification, scientists paid attention to the introduction of polymers in the adsorption process as they composed of area with high surface, which can be used for removing heavy metals ions from contaminated water [15]. In this research, the natural polymer cellulose with amino group was used to extract metal ions from an aqueous solution. Cellulose functionalized with melamine after oxidizing with sodium periodate.

1.3.2.1 Carbon-based adsorbents

Due to their high surface area (500.0–1,500.0 m2g-1), nano porous carbon-based adsorbents, predominantly activated carbons, graphene, and carbon nanotubes are extensively used in the wastewater purification form toxic metals and organic matters. Surface functionalization with functional groups such as hydroxyl, amino, carboxyl, phenyl, and lactone groups can enhance the adsorption efficiency by enhancing the bonding to the heavy metals.

The most well-known carbon adsorbent for metal presents in wastewater and water is the activated carbon. The removal of toxic heavy metal ions from water is only a one example of several environmental applications in which activated carbon is used as adsorbents. The high cost of making coal based activated carbon made the scientist search for alternative in which biochar was invented which is available at lower cost and provide better performance for heavy metal removal for waste water

Biochar was created from many woody biomass, such as agricultural wastes or the byproducts of animal's manure or peanut shell. It is also well known for its variety of functions, such as carbon confiscation, enhance soil fertility, and environmental improvement [16].

Graphene-based substances like graphene oxide or reduced graphene oxide have been researched for potential applications in the removal of heavy metals ever since the advent of nanotechnology. A single sheet of 2D hexagonal carbon is known as graphene, and graphene oxide is created through chemical or thermal reduction methods. Because of its high specific surface area and abundance of surface functional groups,

Cylindrical carbon tubes known as carbon nanotubes are created from one or more graphene sheets. They have easily modifiable surfaces, hydrophobic walls, a substantial surface area, and a clearly defined cylindrical hollow structure. As adsorbent materials, multi-walled and single-walled of carbon nanotubes were explored.

Due to their outstanding electrical, thermal, and mechanical properties, carbon nanotubes and graphene oxide have exciting potential in the field of heavy metal adsorption technology [16].

All carbon adsorbents have the same active surface functional group content, which is a crucial component of the surface chemistry of carbon materials and the adsorption of heavy metals.

The efficacy of heavy metal adsorption is increased by the interaction between the functional groups of adsorbents and the heavy metals. Based on the heteroatoms that are linked to the surface of carbon, functional groups are frequently categorized into three categories: functional groups that include oxygen, nitrogen, and sulfur.

The usefulness and quantity of each type of functional groups will be improved by chemically and physically altering the surface of carbon-based materials by adding the suitable heteroatoms. The presence of functional groups, pore size, or a particular surface area [17].

1.3.2.2 Chitosan-based adsorbents

The second most prevalent polymer that is naturally occurring is chitosan. Chitin occurs naturally in the bodies of some creatures, including many arthropods, fungi, and carbohydrates. Chitosan has the greatest affinity for metals, and this effectiveness is influenced by a number of variables, including its crystalline structure, hydrophobicity, degree of deacetylation, and free amino moiety.

The benefits of using chitosan in the waste water purification process are its low cost, availability, environmental friendliness, antibacterial capabilities, macromolecular structure, renewability, active sites, and high adsorption capacity.

Despite all of these advantages, chitosan-based adsorbents slowly achieve saturation after adsorption, becoming poisonous, and are hardly recyclable. Before discarding and releasing used chitosan adsorbents into the environment, it is crucial to thoroughly recover them. For the efficient and acceptable removal of pollutants from aqueous media as well as the economical and widespread usage of this substance, regeneration of used chitosan adsorbents is crucial [17].

Because of their unique physico-chemical properties, outstanding chelation behavior, high reactivity, high selectivity toward metal ions, high hydrophilicity, and flexible structure of the polymer chain, chitosan-based adsorbents offer remarkable adsorption performance for heavy metals. Chitosan has hydroxyl (-OH) and amino (-NH2) groups, both of which aid in adsorption. There are several mechanisms, including as electrostatic attraction and chelation, that allow metal ions to bind to these fictitious groups for adsorption.

In these mechanisms, the pH level is crucial. The free electron doublet on nitrogen may bind metal cations when the pH is neutral. However, when amine groups are protonated in an acidic environment, the polymer exhibits a cationic characteristic and can bind metal anions. Since metal cations were chelated by ligands in solution, metal anions were created. As a result, the chelation mechanism of chitosan was changed to an electrostatic attraction mechanism on the protonated amine groups of the polymer [18].

Several studies have been conducted on the adsorption of heavy metals from water using chitosan-based adsorbents. Diepoxyoctane cross-linked chitosan beads were used to remove Cr(VI) ions. The coordination of Cr(VI) ions with adsorbent becomes competitive as the pH of the metal solution changes. The pH value for the adsorption of Cr(VI) ions onto diepoxyoctane cross-linked chitosan was 2.

In a different investigation, chitosan microspheres that had been grafted with poly(methacrylic acid) were used to remove Cd(II) ions from an aqueous solution. At pH 5, the greatest Cd(II) uptake value was attained.

Chitosan flakes were used to remove Cu(II) from an aqueous solution. The results showed that increasing the concentration of chloride ions in the solutions increased the adsorption capacity. At pH 5.0-6.0, the greatest capacity for Cu(II) adsorption was achieved. [18].

1.3.2.3 Zeolites

One of the mineral adsorbents that has been suggested as a viable option for water purification is zeolites. Zeolites can be created artificially or obtained from nature via silicate minerals. In adsorption, catalysis, the building industry, agriculture, soil remediation, and energy, natural zeolites have a wide range of uses.

Zeolites are tetrahedral, three-dimensional aluminosilicates with potassium, calcium, and sodium that also contain silicon and aluminum that is surrounded by oxygen. Zeolites were assumed to be effective adsorbents due to their ion exchangeable [19].

The three main components of zeolite structure are the aluminosilicate framework, exchangeable cations, and zeolitic water. The aluminosilicate framework, which is the most common and stable material, determines the type of structure. Water molecules linked to framework ions and exchangeable ions via aqueous bridges may exist in large hole gaps. Water can also act as a conduit for cations to exchange [19].

For the removal of metal ions zeolite can be used, it is made by the reaction of the organic cations ethylhexadecyldimethylaminonium (EHDDMA) and cetylpyridinium (CETYL).

The most well-known property of zeolites is their ability to exchange ions with an external medium. Ion exchange is a process that is isomorphous. Natural zeolite's ion-exchange properties are influenced by its structure, ion size and shape, anionic framework charge density, and external electrolyte solution ionic charge concentration.

Clinoptilolite, mordenite, phillipsite, chabazite, stilbite, analcime, and laumontite are a few of the frequent natural zeolites; however, offretite, paulingite, barrerite, and mazzite are uncommon. The most prevalent naturally occurring zeolite in the world is clinoptilolite.

Synthetic zeolites have a higher cation exchange capacity (CEC) and faster reaction kinetics than their natural counterparts, which makes them more efficient at removing ions. Zeolites can be modified using a variety of methods to increase their adsorption capacity when used to treat wastewater. These methods include chemical activation, thermal activation, surface modification, and the creation of unicationic forms of the material.

However, the economic cost-effectiveness of modified zeolites and the material and financial costs of manufacturing in the usage of the zeolite should be taken into account when choosing the appropriate application.

When zeolites crystallize, they create extraordinarily uniform holes and channels that only permit certain ions and water molecules to pass through. Because of their ability to absorb substances, zeolites are microporous and have mesoporous features [20].

1.3.2.4 Clay

On the surface of the planet, a particular kind of tiny particle is called clay. Water, alumina, silica, and worn rocks make up the majority of it. Clay minerals are also good adsorbents because they contain exchangeable cations including Na+, Ca2+, and K+. Because clay has a negative charge from the presence of silicate (Si+4), it has a greater capacity for adsorption. In clay minerals, which are primarily phyllosilicate minerals, an octahedral aluminum sheet is surrounded by one or two tetrahedral silica sheets. Each silicon atom is surrounded by four hydroxyl groups in the Si2O6(OH)4 unit found in the tetrahedral sheets [21].

The mechanisms for the adsorption of heavy metals by clay adsorbents are ion exchange, surface complexation, and direct bonding of heavy metal. Clays can also be pretreated to improve their capacity to absorb heavy metals. Clay that has been pretreated has more pores, surface area, and acid sites on its surface. This enhances the efficacy of non-ionic organic material adsorption after treatment or modification.

The fineness of the particle size, rigidity, good flexibility, associativity, acceptable shrinkage, high resistance, and capacity for surface decoration are the physical properties of clays. Small particle sizes and high specific surface areas of clay are produced by complex porous architectures, allowing for physical and chemical interactions with dissolved minerals.

Clay minerals can be divided into 1:1 or 2:1 category. One tetrahedral sheet and one octahedral sheet that are uncharged and have a hydrogen link between the layers are the building blocks for 1:1 type clays like kaolinite and serpentinite.

Talc, vermiculite, and montmorillonite are examples of 2:1 clay. They are composed of an octahedral sheet sandwiched between two tetrahedral sheets that have a negative charge and can be joined by individual cations or by positively charged octahedral sheets.

Kaolinite, montmorillonite, and illite are three significant mineral groups that make up clay. Nearly all clays have one or more people from one of these three groups.

Montmorillonite, a hydrous magnesium calcium aluminum silicate, is how bentonite was created (a type of smectite). It is made up of very minute particles formed from volcanic ash, either Na-montmorillonite or Ca-montmorillonite, and is a highly colloidal and plastic clay. Montmorillonite clay has the smallest crystal size of any clay and has the highest surface area and cation exchangeability, which is why it has a strong capacity for adsorption.

The primary component of common clay, illite, is found in limestone and is found in a variety of groupings, including hydrous micas, phengite, brammalite, celadonite, and glauconite (a green clay sand),

The majority of ball clay, a fine-grained, highly malleable sedimentary clay with commercial value, is composed of kaolinite, mica, and quartz [22].

1.3.2.5 Lignin

Plant cell walls must contain lignin, which is the second-most prevalent biopolymer in nature after cellulose. A wide range of naturally occurring aromatic polymers created by the oxidative coupling of precursor monolignols are referred to as "lignin." Coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol are the typical monolignol precursors of lignin. Because they significantly influence the chemical and physical properties of lignin, such as its reactivity, hydrophilicity, and functionality, the hydroxyl groups in the lignin macromolecule are vital.

Lignin-forming substances act as cellular glue, holding together the individual fibers and strengthening the plant tissues. Depending on the type of plant, where it grows, and how long it grows, lignin has different structures and repeat units. The parent plant, as well as environmental and developmental factors, have a major impact on the molecular weight of any specific lignin. The characteristics of the lignin are significantly influenced by the extraction procedure. Grass lignin, hard wood lignin, and soft wood lignin are three broad categories for plant lignin. Grasses contain the least amount of lignin, whereas soft wood contains more than hard wood.

Due to the increased demand for renewable, biodegradable raw materials for the production of adsorbent polymers, lignin has emerged as a viable substitute for natural biopolymers due to its high availability, stability, low cost, biodegradability, and CO2 neutrality.

The sorption capability was caused by the lignin structure's inclusion of phenolic and carboxylic groups. As a result, using lignin as metal adsorbents in water treatment is a successful and sustainable method.

Despite the fact that lignin is used as an adsorbent to remove a variety of pollutants, a modification process is required to boost lignin's affinity for certain water contaminants. The specific surface area, pore size distribution, pore volume, and surface functional groups of lignin were some of the characteristics that dominated the adsorption of heavy metals by lignin [23].

Because of the reactivity of the primary phenol hydroxyl groups, the active hydrogen atoms at the para- and ortho sites next to the phenol groups, the alcohol hydroxyl groups, and the side-chains, lignin is susceptible to modification. A variety of chemical processes, including acylation, alkylation, carboxymethylation, etherification, esterification, crosslinking, condensation, and graft copolymerization, could be used to add different active groups to these locations.

The primary functional groups for the adsorption of heavy metal ions can be divided into a number of categories, including those that contain oxygen, sulfur, nitrogen, and phosphorus.

Two significant types of lignin that are easily accessible on an industrial level are lignosulfonates and kraft lignin. Kraft lignin produces over 85% of the world's lignin [24].

1.3.2.6 Seaweed

Thousands of different types of microscopic, multicellular, marine algae are referred to as seaweed or macroalgae. Due to their various special qualities, such as ecosystem balancing, lowering eutrophication for nutrient management, or bioremediation, seaweeds are used in a variety of industrial applications. Seaweed extract is consumed as a source of fresh food, utilized as a biobased fertilizer for crops, and decomposes anaerobically to produce biogas that is high in energy. Most commonly, seaweeds are eaten raw or utilized to produce commercially important phycocolloids. Natural polymer from seaweed is another source that is added to the formulations of conventional plastics to produce biodegradable plastics. Additionally, they have been employed domestically as a source of protein that may be used to produce a range of food items with added value as a source of flavor, medication, and food for animals.

They are often separated into three categories according to the color of the thallus and are classified as Chlorophyta (green algae), Rhodophyta (red algae), Heterokontophyta, and class Phaeophyceae (brown algae) [25].

In contrast to its use in a variety of industries, seaweed has been extensively researched and used as an adsorbent to replace functional activated carbon in sewage treatment. Numerous studies have shown that the polysaccharides in their cell walls influence both their high sorption capacity and selectivity for different metal cations. Their cell walls are fundamentally made of cellulose-based fibrils, an amorphous framework of sulfated galactans composed of carrageenans and agar in red algae and alginates or alginic acid and fucoidan in brown algae. [26].

Depending on the chemical species used, the source of the biomass, and the method used to prepare it, the various mechanisms involved in the biosorption of heavy metals vary in quality and quantity. Some of these mechanisms include crosslinking for reinforcement, complex formation, electrostatic interaction, and ion exchange, which is the most important mechanism.

Some of the factors that influence a seaweed cell surface's ability to absorb are the number of functional groups in the algae matrix, the coordination number of the metal ion that will be adsorbed, the conductivity of binding groups for metal ions, the formation of complexes, the affinity constants of the metal with the functional group, and the chemical state of these sites.

The carboxyl, hydroxyl, sulfate, phosphate, and amine groups found in the cell wall matrices of brown and green algae play a significant role in the binding of metals. By using an ion-exchange mechanism between heavy metals and intrinsic light metal ions like Ca^{2+} and Mg^{2+}, as well as Na^{+} and K^{+}, it has been discovered that the presence of these functional groups plays a dominating role in the interaction between metals and algae [26].

In order to improve the surface structure of seaweed cells and provide more binding sites, physical and chemical methods are being researched.

.1.4 Cellulose polymer

Cellulose is considered the most abundant natural basedpolymers, which is distributed in plants, algae, fungi, bacteria, several marine animals. This organic polymer have a formula $(C_6H_{10}O_5)_n$ .Cellulose was used a natural based adsorbent that has been used in the wastewater purification process due to its low cost, availability, and environmental friendliness [27]. Cellulose can be used in many applications as it can be converted into different polymers, as is the case in this research.

Since its initial discovered and isolated by Anselme Payen in 18382, cellulose has undergone significant physical and chemical study. In fact, new insights into its biosynthesis, assembly, and structural characteristics have inspired several scientific research across a wide range of fields.

In this research, cellulose was obtained from the Olive industry solid wastes (OISW) by a method that was designed and created at An-Najah University (Palestine). Olive industry produces two kinds of waste materials, the first is a black liquor known as Zebar, and a solid material known as Jeft. Liquor contains bio-oxygen (BO) and has a high concentration of chemical oxygen , it is alos toxic polyphenols [15].

The olive industry represents one of the most important industrial process. The risk of this industry waste is a hundred times greater than the effects of drain water dispensed by local in urban areas, and may contribute to the deterioration of its quality, and loss of vegetation cover by damaging the soil. In some countries, OISW is usually burned which results in the release of CO_2 to the environment, while the liquor is disposed of through the darin, which inversely affects the nature.

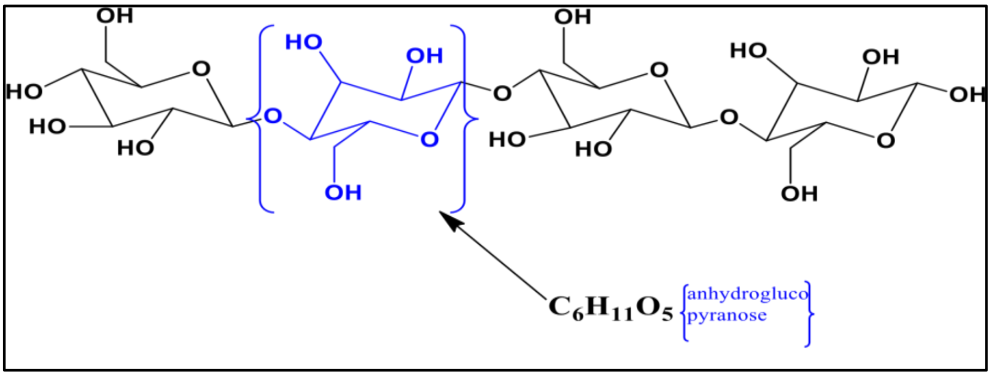
As a result, finding strategies to exploit these contaminants and turn them into usable resources that benefit the agricultural economy is essential.

1.4.1 Chemical structure of cellulose

Cellulose is a fibrous, strong, and water swellable but -insoluble polymer. Cellulose is composed of D-glucose units, with the monomers are connected by ß-1,4-glycosidic linkage.

Scheme 1.1

Cellulose Structure

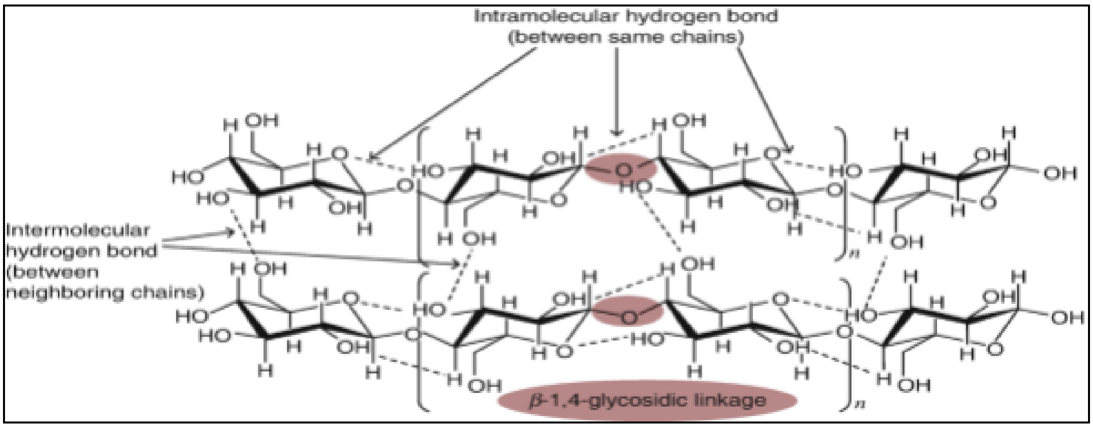


Each D-anhydro glucopyranose unit carries three OH (two secondary and one primary). The hydroxyl groups can react like small molecules with primary and secondary alcohols [28].

These multiple hydroxyl groups interact with oxygen atoms nearby or within the same chain to form hydrogen bonds, which causes the chains to come into contact with one another and create microfibrils with high tensile strength. Heavy metal ions are attracted to hydroxyl groups.

Scheme 1.2

Hydrogen bonding in cellulose macromolecule.



Crystalline and amorphous regions can both be present in cellulose fibrils. The crystalline structure of cellulose affects its properties. For example, the flexibility of cellulose decreases as the amount of crystalline cellulose increases due to a strong hydrogen bonding network.

There are various allomorphs of cellulose due to the wide orientation of the hydrogen bonding networks. Flexible cellulose nanofibrils are created through enzymatic or chemical oxidation of cellulose fibrils. Short stiff cellulose nanocrystals will be produced if the fiber is hydrolyze with a an acid (few nm in length)

1.4.2 Nanocrystalline cellulose (NCC)

Recently, nanomaterials has become one of the most prominent fields that are used to develop new materials that have amazing performance in the field of industry, where nano-sized materials are used and benefited from in many aspects, especially in water purification, as is the case in activated carbon [29].

In comparison to bulk particles, nanoparticles have a higher specific surface area, and they can be functionalized with different chemical groups, increasing their affinity for contaminants.

However, although these materials have many benefits, there are also negative aspects, such as that they are permeable and expensive and have an impact on the environment. Therefore, a search was made for low cost, renewable nanomaterials and environmentally friendly. The cellulosic polymer showed its properties of the nanoscale materials as it is the major component of wood which is a renewable and abundant resource. Therefore, cellulose has received attention in the field of nanotechnology [30].

Several cellulose-based materials and derivatives have yet to be investigated in wastewater purification, despite tremendous improvements in nanocellulose adsorbents.

Nanocrystalline substances are single- or multi-phases polycrystalline solids with a few nanometers size, usually less than 100 nm.

1.4.3 Cellulose modified chemically for removing heavy metals

Physical or chemical modification of cellulose reduces the crystallinity by reducing the strength of hydrogen bonding and the OH of cellulose repeat unit will be exposed to chemicals [31].

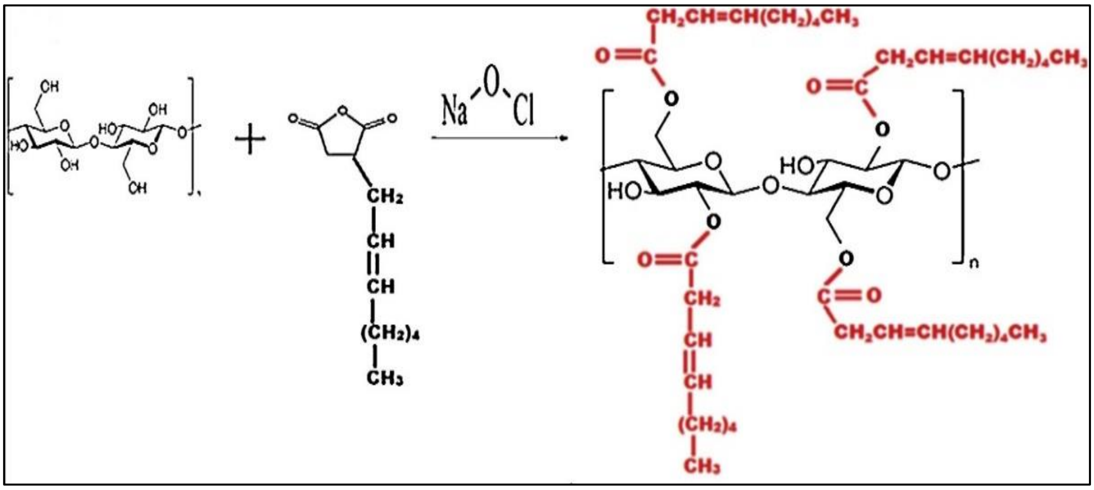
Primary methods for cellulose modification:

1) Cellulose cross linking to make cellulose insoluble in water but swells and form gel.
2) Cellulose grafting which can be done by polymerizing a monomers on cellulose repeat unit or adding new functionality [32].

Various cellulose polymers modified with new functionalities were prepared, several cellulose modification methods are reported in the literature such as esterification with sodium hypochlorite and octenyl succinic anhydride. This added a carbonyl group pendant group to cellulose polymer which is known to have high for Pb(II) (Scheme 1.3) [33].

Scheme 1.3

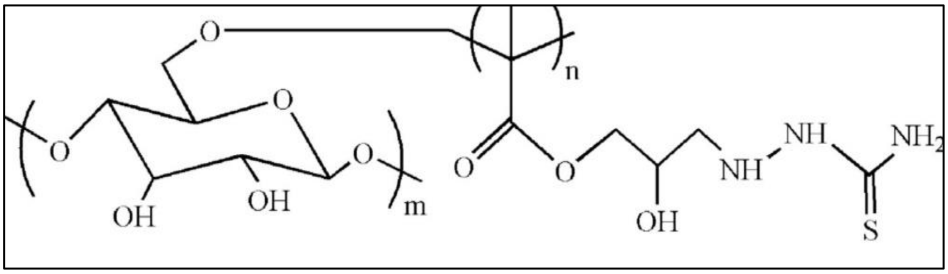
Cellulose modified with fatty ester.



In published work showed that carboxyl group can be added to cellulose repeat unit cellulose by grafting with the glycidyl methacrylate using ceric ammonium nitrate as a catalyst, then functionalizing the carboxyl group with thiosemicarbazone which contains amino and C=S groups (Scheme 1.4). The polymer was used to remove heavy metals from water. The polymer showed excellent affinity for Hg(II) and Cd(II). The adsorption obeyed the kinetic model pseudo second order and Langmuir isotherm models [34].

Scheme 1.4

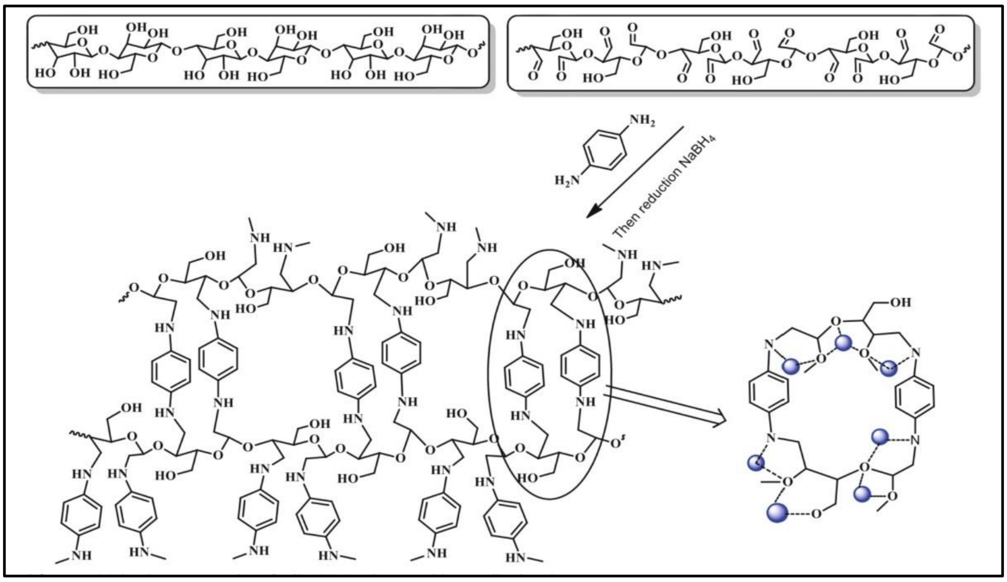
Cellulose modification.



A new adsorbent material based on modified cellulose was prepared by bridging NCC chains with p-phenylenediamine to produce mime functionality which was then reduced to crosslinked cellulose with amine functionality by reacting it with $NaBH_4$ (Scheme 1.5). The polymer showed excellent efficiency toward $Cu^{2+}$and Pb^{2+}. The adsorption mechanism followed the pseudo-second order kinetic. [34]

Scheme 1.5

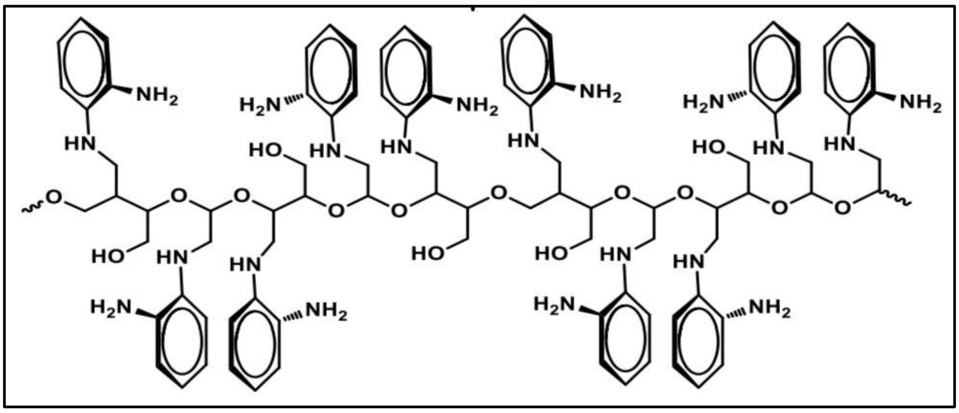
Crosslinked cellulose with diamine functionality



In another published work cellulose was derivatized with o-phenylenediamine (Scheme 1.6) to create a structure with bidentate ligand. It showed excellent removal of Fe(III) and Pb(II) form water and high efficiency toward adsorption of toxic metal ions from sewage wastewater. [35]

Scheme 1.6

Cellulose with bidentate functionality.



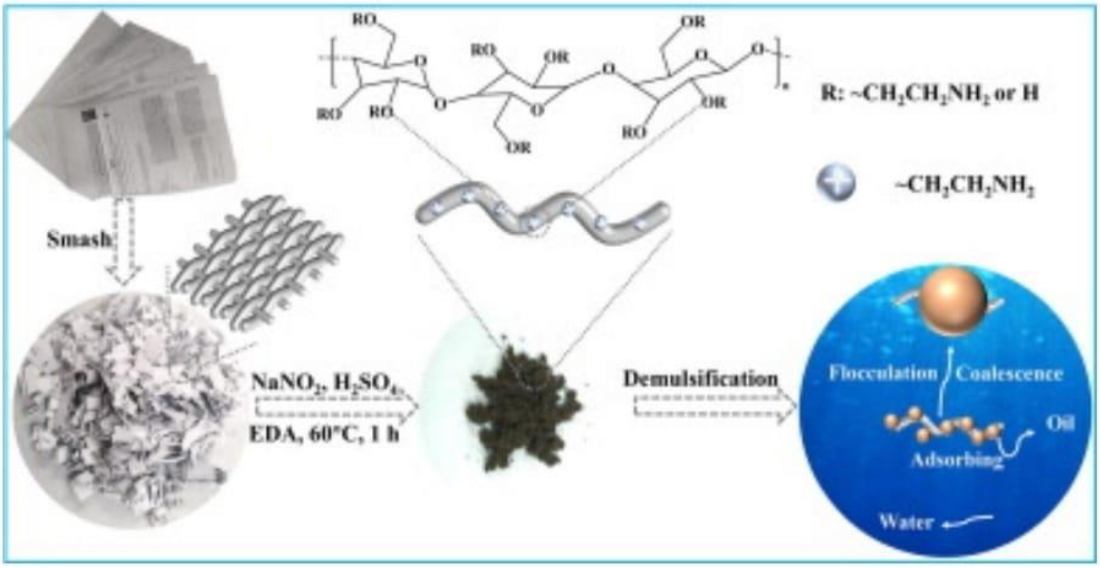
Magnetic nanocrystalline cellulose was prepared from cellulose and used as selective removal of dye methylene blue from wastewater .[36]

In this work cellulose was selected as base polymer for making adsorbent for toxic metals present in water. It was modified by oxidation and functionalization with melamine.

In a reported study cellulose derivatized with amine-functional group was prepared (Scheme 1.7) and used in wastewater purification the cellulose was extracted from collected wastepaper. The modified cellulose showed excellent efficiency toward oil present in wastewater the total removal rate reached about 99.2%. It was shown that, the modified polymer could be used under the high salt, acidic, alkaline or conditions. [36]

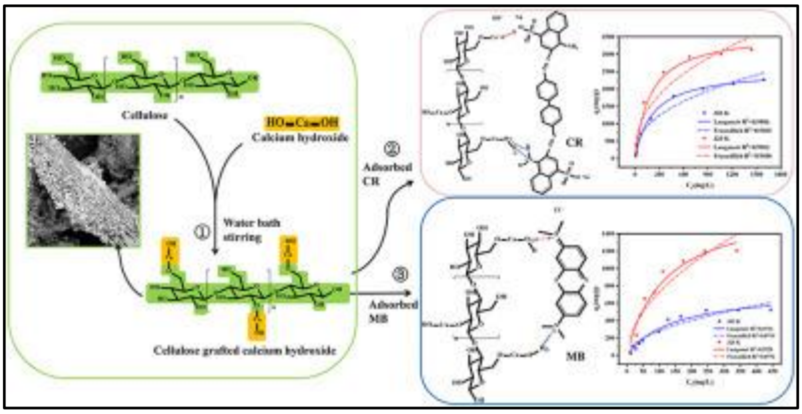
Scheme 1.7

In a another study amphoteric cellulose-grafted with calcium hydroxide was prepared (Scheme 1.8) for use in wastewater purification. The maximum adsorption efficiency and maximum adsorption capacity of the grafted cellulose at 303.0 K reached about 92% for the dye Congo red and 84.5% for methylene blue. In addition, the amphoteric adsorbent was reused many times, Therefore, cellulose modified with calcium hydroxide is an efficient amphoteric adsorbent for wastewater purification.[37]



Scheme 1.8

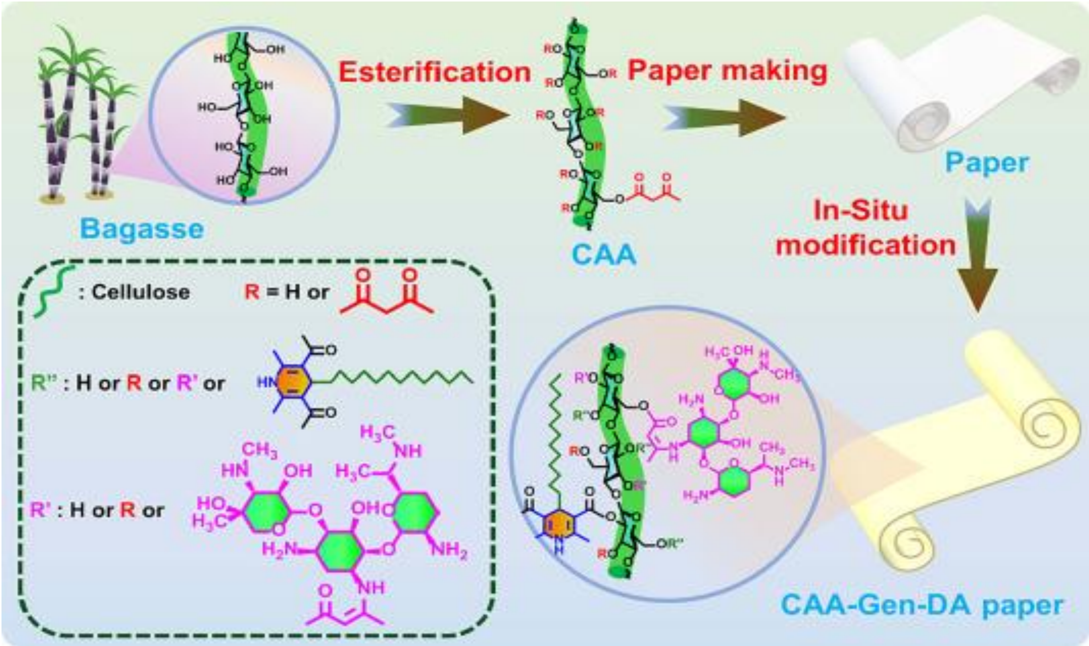
A representative scheme shows the interaction of the grafted cellulose with dyes.



Cellulose with acetoacetyl groups was synthesized by a heterogeneous transesterification method. The fluorophore and gentamicin sulfate functionalities were bonded to the cellulose using the reaction discovered by Hantzsch to produce enamine bond (Scheme 1.9). The produced cellulose showed excellent multifunctional properties like antibacterial, fluorescence property and hydrophobic property in addition to wastewater treatment. [38]

Scheme 1.9

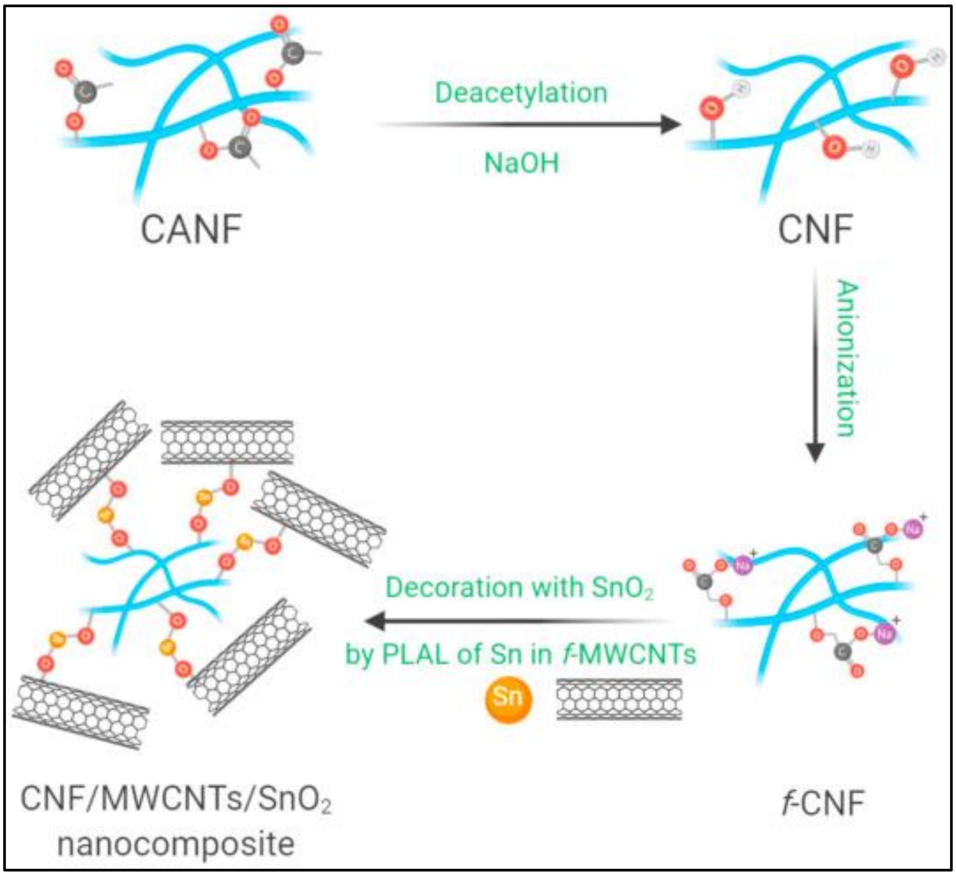
A diagram shows the preparation of the multifunctional cellulose obtained from biogases.



Cellulose nanofiber hybrid with multi-walled carbon nanotubes and tin oxide (SnO_2) forming CNF/MWCNTs/SnO_2 nano structure (Scheme 1.10) was prepared in the form of fiber membrane by electrospinning and laser ablation methods and used in removal of Cu (II) ions from water. The structure was confirmed by infrared red and X-ray diffraction. The adsorption of the nano structure toward Cu^{2+} ions was investigated as a function of contact time, pH, contact time and concentration of adsorbent and Cu(II) to ge .

Scheme 1.10

the synthesis of CNF/MWCNTS/SnO2 nanostructure.t to the optimum conditions.[39]



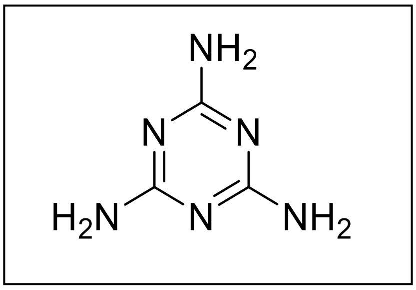
1.5 Melamine (Mel)

Melamine with the IUPAC name 2,4,6-triamino-1,3,5-triazine is an organic material, its chemical formula is $C_3H_6N_6$ and its molecular weight is 126.12 g/mol. It was prepared by reacting potassium thiocyanate with ammonium chloride at high temperature. Also can be prepared by various methods such as heating thiourea, guanidine carbonate, cyanamide, or dicyandiamide. Ammeline and cyanuric acid can be generated from Melamine. Besides, those derivatives are co-products produced during melamine synthesis. [40]

Melamine is commonly used in food products to increase the apparent protein concentration which found to cause reproductive damage, or kidney stones, bladder damage and bladder cancer [41].In addition, it is often reacted with formaldehyde to produce high quality plastics used in manufacturing kitchenware, whiteboards, and commercial filters .

Scheme 1.11

Chemical structure of Melamine



In this study, melamine was bonded to cellulose nanocrystalline to generate a cross-linked 3D cellulose polymer. Melamine was selected because several amino groups which makes excellent chelating agent for metal ions.

Work scope

The general objective of the current work is to synthesize nanocrystalline cellulose melamine Schiff base as toxic metal ions adsorbent especially those present in wastewater.

The sub objectives include:

- Convert cellulose generated from the waste material of the olive squeezing factory to nanocrystalline cellulose (NCC).
- Develop a chemical method to oxidize cellulose to cellulose diladehyde.
- Develop a method for converting NCC to nanocrystalline cellulose melamine Schiff base (NCC-Mel).
- Characterize the polymer by various spectroscopic methods.
- Evaluate the performance of the generated (NCC-Mel) as a metal adsorbent present in wastewater.

Chapter Two

Experimental

2.1 Methods

The instruments used in this project were a water heating bath furnished with a shaking equipment (Daihan Labtech, 20 to 250 rp per min Digital Speed Control), pH meter (Jenway, 3510), Inductively Coupled Plasma Mass Spectrometer ICP/MS (ICE 3xxxC113500021 v1.30).

The concentrations of Lead ion after and before adsorption were determined by Flame Atomic Absorption Spectrometer (FAAS) (ICE 3000 series AA System, Thermo Scientific).

The functionality present in the polymer were located by Fourier transform/infrared spectrometry (FT-IR) (Thermo Fisher Scientific comapny (MA, USA) equipped with the Smart Split Peaks Hemi Micro ATR accessory (International Crystal Laboratories, Garfield, NJ, USA).

The IR parameters were resolution 4.0 cm^{-1}, range from 600 cm^{-1} to 4000.0 cm^{-1} and with 128 scans.

All analyses were carried out in triplets and the mean of the trials was calculated and reported. The metal ions present in real sewer samples were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). There concentrations were determined before the treatment with the adsorbent and after.

2.2 Materials

The analytical grade chemicals and solvents used in this investigation were utilized exactly as they were obtained. Aldrich Chemical Company provided the reagents for this project (Jerusalem).

All solutions used in the current work were prepared using deionized water. Cellulose polymer was purified by a by a bench process created at An-Najah University [42].

2.3.1 Generation of nanocrystalline cellulose (NCC):

A 10.0 g sample of cellulose powder obtained from the industrial waste of olive oil waste material was place in a beaker suspended in a 200 mL deionized water. The suspension was mixed magnetically for two hours for activation. Then, 10.0 g of concentrated sulfuric acid was added to the cellulose mixture and sonicated for 2.0 hr. at room temperature. Produced NCC was collected by centrifugation, then rinse three times with water (200 ml x 3) and dried at room temperature.

2.3.2 Nanocrystalline cellulose (NCC) with aldehyde functionality

Nanocrystalline cellulose (10.0 g) was added to a 1 L beaker containing 500 mL of deionized water followed with $NaIO_4$ (16 g, 0.093 mol).The produced mixture was wrapped with aluminum foil to keep the light away, reaction mixture was mixed by a mechanical mixer for 24 h at a 40 °C and, after which the produced oxidized cellulose (dialdehyde) solid was gathered by suction filtration.

2.3.2.1 Degree of substitution

A sample of the cellulose aldehyde (1.0 g) was mixed with a 50.0 mL of 2-propanol, stirred for 10.0 min then 10 mL of deionized water was added. The pH of the suspension was adjusted to pH of 3.5 using 5.0% HCl and stirred for another 30 min.

A 20.0 mL solution of $NH_2OH.HCl$ (hydroxylamine hydrochloride), 5.0% by mass) in water was prepared. The pH of the mixture was adjusted using 5% HCl to 3.5.

The two above solutions were combined and mixed for 3.0 hr. then neutralized with a NaOH (0.5 N) solution to a pH of 3.5.

The equation shown below was used to determine the aldehyde content:

$$[Ald] = (V_{NaOH} x N_{NaOH} x 162) / W_{OC} \qquad \text{Eq.1}$$

Where

[Ald]: degree of substitution (mmol per anhydroglucose unit).

V_{NaOH}: volume of NaOH (mL).

N_{NaOH}: normality of the sodium hydorxide (eq/L).

W_{OC}: oven dry weight of cellulose oxidized (g).

2.3.2.2 Functionalization of cellulose aldehyde

Cellulose polymer with aldehyde functional group prepared above was reacted with Melamine to synthesize the target polymer (NCC-Mel) with imine and amine functionalities.

A 1.00 g (0.0061 mol) of cellulose aldehyde and 2.05 g of Melamine (0.00561 mol) were suspended in a 50 mL of methyl alcohol as solvent in a flask (100 mL) equipped with a condenser and magnetic bar. The flask contents were heated at about 70 ℃ for 24 hr. The produced solid was collected by filtration and rinsed with methanol 3 x 50 mL, then dried at room temperature.

2.4 Standard solutions of Lead (II)

A stock solution of Pb (II) in deionized water with a 1000 ppm concertation was made by dissolving 0.16 g of $Pb(NO_3)_2$ (331.21 g/mol) in a 100 mL deionized water in a volumetric flask. The stock solution was used to prepare standard solutions of Pb (II) with various concentrations ranging from 1.00 to 20.00 ppm.

The adsorption experiment was performed on standard solutions using a batch experiment, the effect of the following parameters on adsorption efficiency were evaluated: time, initial concentrations, dosage, temperature and, pH.

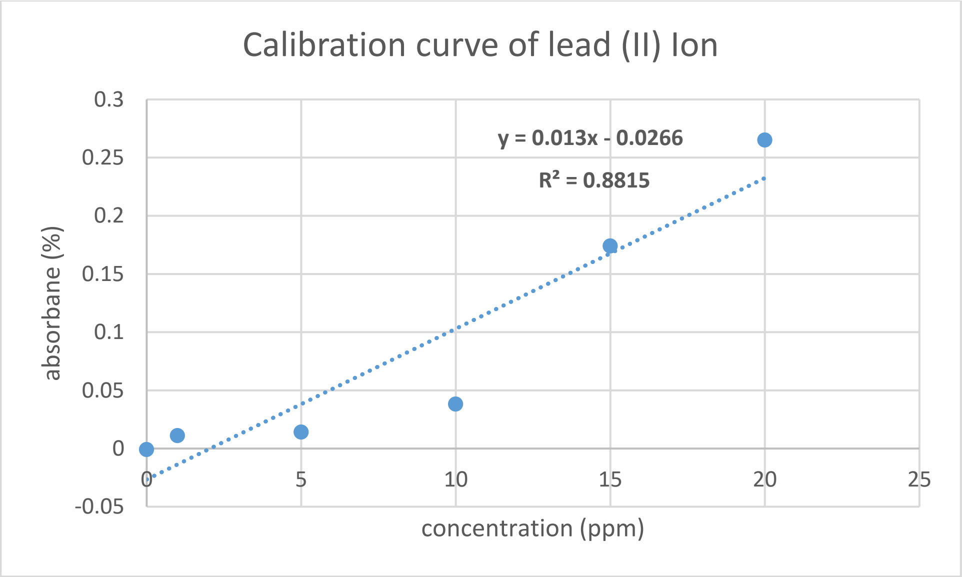
The initial and final concentrations of metal ion Pb (II) was determined by flame atomic absorption spectroscopy (FAAS).

2.5 Calibration curve

The calibration curve for Pb (II) prepared from the standard solutions was created by Flame atomic absorption spectroscopy (FAAS) by measuring absorbency of the standard solutions (Figure 2.1).

Figure 2.1

Calibration curve of lead (II)



2.6 Adsorption of Pb (II) by batch process

A known weight of (NCC-Mel) was mixed with a known volume of a standard solution of Pb (II) and stirred. One of the following parameters was changed while the others were kept constant. The parameters are pH value, time, Pb(II) initial concentration ,adsorbent dosage and temperature. This was performed to determine the ideal adsorption conditions.

2.6.1 Effect of adsorbent dosage

The optimum amount of adsorbent cellulose (NCC-Mel) on the adsorption efficiency of lead (II) ions was studied using various amount of adsorbent (5.0, 10.0, 50.0, 75.0 or 100 mg) while the volume of Pb (II) solution was 10.0 mL with a 20.0 ppm concertation, the pH of the solutions was adjusted to 7.00. The solutions were mixed in a water bath at a 25 °C, for 25 minutes.

The final concentration of Pb (II) in the collected filtrate was determined by FAAS.

The obtained concentrations are summarized in Table 2.1. The highest efficiency was at 75.0 mg.

Table 2.1

Effect of the adsorbent dosage.

Dose (mg)	Percentage removal of Pb(II) (%)
5.0	70.5
10.0	69.5
50.0	80
75.0	82.5
100.0	79.5

2.6.2 Effect of metal ion concentration

The effect of Pb(II) concentration on the removal efficiency was determined as follows: an adsorbent dose of 75.0 mg was added to five containers with different concentrations of Pb(II) ranging from 1.0 to 20 ppm, each containing 10.0 mL at a pH of 7.0, mixing time was 25 min at a temperature of 25 $^{\circ}$C

All solution were then filtered using a syringe fitted with a 45-micron filter.

Then, the final lead ion content in each filtrate was determined using FAAS, the obtained results are summarized in Table 2.2. The highest efficiency occurred at 5.0 ppm solution.

Table 2.2

Effect of the initial concentrations of lead(II) ions

Conc. (ppm)	Percentage removal of lead (II) (%)
1.0	87.5
5.0	88.5
10.0	86.5
15.0	81
20.0	82

2.6.3 Effect of mixing Time

The mixing time effect on adsorption efficiency was also determined. Five standard solutions, 10 mL each with a 20.0 ppm concertation were loaded with 75 mg sample of the polymer. The solutions were mixed at various times (5.0, 10.0, 15.0, 20.0 and 25.0 min), each sample was filtered as above, and the residual concentration of the final lead ion concertation was measured by FAAS.

The results are shown in **Table 2.3**. The optimum mixing time was about 10 min.

Table 2.3

Effect of contact time

Time (min.)	Percentage removal of lead (II) (%)
5.0	64
10.0	79
15.0	75.5
20.0	74.5
25.0	71.0

2.6.4 Effect of pH value

The pH effect was studied in the range of 2.0 to 12.0 to determine the effect of pH on the adsorption efficiency. The pH values adjusted using 0.1 M HCl and 0.1 M NaOH solutions. Standard solutions with the following criteria were prepared, 75 mg of adsorbent dose was added to a 10.0 mL of solution with 5 ppm the adsorption was performed at temperature of 25 ºC for 10 minutes.

The filtrate obtained from each run was analyzed by FAAS.

The results are shown in Table 2.4. The highest adsorption was obtained at a range of pH (6.5-7.5)

Table2.4

Effect of the pH value.

pH	Percentage removal of lead (II) (%)
2.0	15
3.0	25
7.0	66.5
9.0	54.5
12.0	39.5

2.6.5 Optimum temperature

Five standard solutions were prepared, each with 10.0 mL contains 75 mg of the polymer and 5 ppm of lead (II) at a pH value of 7.0. All solutions were shaken in a water bath at a temperature ranging from 15.0 to 55.0°C for 10 min.

As shown before, the final concentration of Pb (II) in each solution was determined using FAAS

The results obtained are shown in Table 2.5. Highest removal of Lead (II) was obtained at a range of (25-35 ºC).

Table 2.5

Effect of temperature

Temp. (ºC)	Percentage removal of lead (II) (%)
15.0	73.5
25.0	75
35.0	75.5
45.0	71.5
55.0	73

2.7 kinetics study

The kinetics of the adsorption by the modified cellulose polymer (NCC-Mel) was studied.

The adsorption kinetics was carried out on standard solutions under the optimal conditions determined.

A 75.0 mg sample of the cellulose polymer was added to a 10.0 mL solution with a 20.0 ppm of lead (II) at pH of 7.0 and shaken for 10.0 min at room temperature.

The adsorption rate was determined and compared to the theoretical values obtained by pseudo-kinetic models (first model and second order model). Parameters such as K, q_e and R^2 values of the pseudo first and pseudo second order kinetic models of the adsorption were obtained and the theoretical and obtained experimentally q_e values were matched.

2.8 Adsorption thermodynamics

To determine the spontaneity of an adsorption by the polymer, it is required to investigate its thermodynamics parameters such as the change in entropy (ΔS), enthalpy (ΔH), and change in free energy (ΔG).

The relationship between the thermodynamic factors is summarized below [43] :

$$\Delta G = \Delta H - T\Delta S \qquad \text{Eq. 2}$$

Where; ΔG is the Gibbs free energy change in KJ.

ΔH is enthalpy change in KJ, and

ΔS is the entropy change in KJ/K

ΔG is related to K_d (thermodynamic equilibrium constant) by the equation shown below (Eq. 3):

$$\Delta G = -RT\ \mathrm{In}K_d \qquad \text{Eq. 3}$$

R is the gas constant (8.314 $J.mol^{-1}.\ K^{-1}$)

K_d is the thermodynamic equilibrium constant that = q_e/C_e and T: the absolute temperature in K.

The following equation can be obtained from Eq. 3:

$$\text{Ln } K_d = \Delta S/R - \Delta H/R \qquad \text{Eq. 4}$$

Plotting In K_d vs. (1/T) in the Van't Hoff equation produces a straight line with the slope of - $\Delta H/R$, and an y-intercept of ($\Delta S/R$).

2.9 Purification of sewage water

In the current study, an actual wastewater sample that was obtained from the Water Center at An-Najah National University in Nablus, Palestine, was used. The Water Center at An-Najah National University used ICP-MS to measure the amounts of transition metal ions in the sewage sample.

Two samples each with a 10 mL of wastewater were treated with 75.0 mg of adsorbent at the optimum conditions (10 min at 25^{o}C at a pH of 7). A sample from each mixture was filtered through a 0.45 µm filter connected to a plastic syringe then analyzed by ICP-MS concertation of metal ions that leftover.

Chapter Three

Results and Discussion

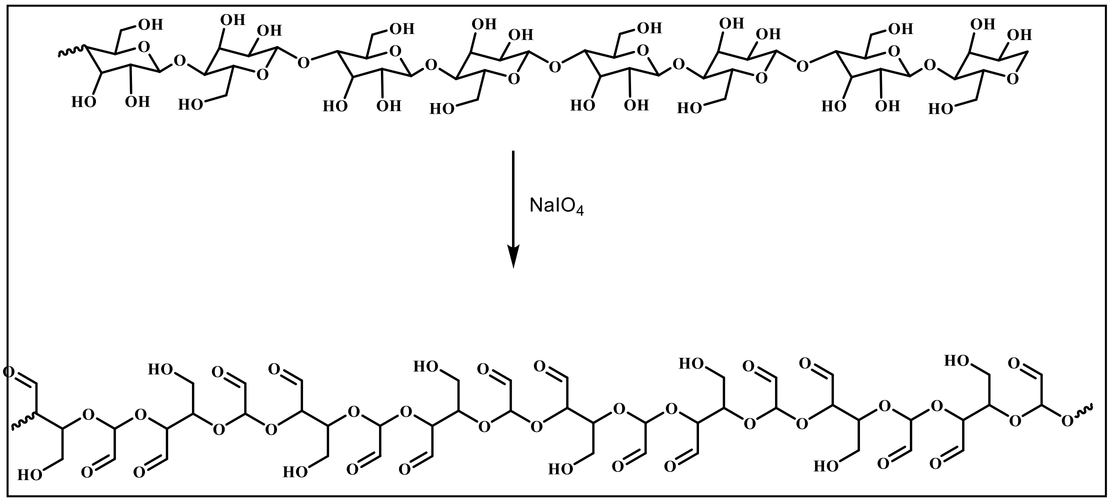
3.1 Preparation of Cellulose-2,3-Dialdehyde

Oxidation of Cellulose to cellulose aldehyde (Cell-2,3-DA) was carried out using ($NaIO_4$) reagent as shown in figure 3.1. Periodate is known to oxidize vicinal dihydroxyl group, so it was selected to oxidize the C-2 and C-3 hydroxyl groups in the repeat unit of the cellulose polymer chain to aldehydes reported by Jackson and Hudson, the amount of reagent and the reaction conditions were optimized to obtain highest rate of oxidation [44].

Cellulose was oxidized with a periodate ($NaIO_4$) inwater, the reaction mixture was completely covered with aluminum foil from light. Periodate coordinates to the C_2 and C_3 adjacent hydroxyl group then cleavage at C_2-C_3 bond occurs as a results of that an oxidation of the adjacent hydroxyl groups on C2 and C3 were converted dialdehyde occurs (figure 3.1)

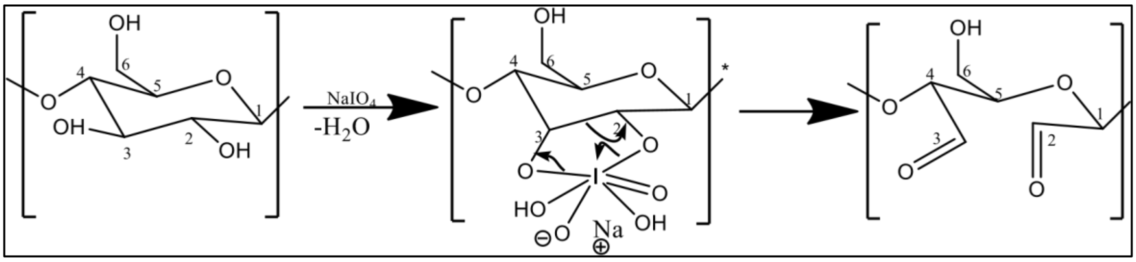
Scheme 3.1

Oxidation of nanocrystalline cellulose (NCC) to cellulose with aldehyde group



Scheme 3.2

Conversion of NCC to Cellulose aldehyde



3.1.1 Degree of substitution (Aldehyde Content)

Hydroxylamine-hydrochloride method was used to determine degree of substitution of aldehyde per anhydro glucose repeat unit, that was done by converting the oxidized cellulose to oximes by treating it with (NH_2OH) hydroxylamine. hydrochloride as shown in the experimental chapter.

The reaction of cellulose aldehyde with hydroxylamine generates the HCl, the amount of HCl generated was determined by titration with NaOH solution with 0.5 N concentration to the end point of 3.5 pH and the aldehyde content was calculated by Equation 1:

$$[Ald] = (V_{\mathbf{NaOH}}\ N_{\mathbf{NaOH}} x\ 162.0)/W_{\mathbf{OC}} \qquad \text{Eq.1}$$

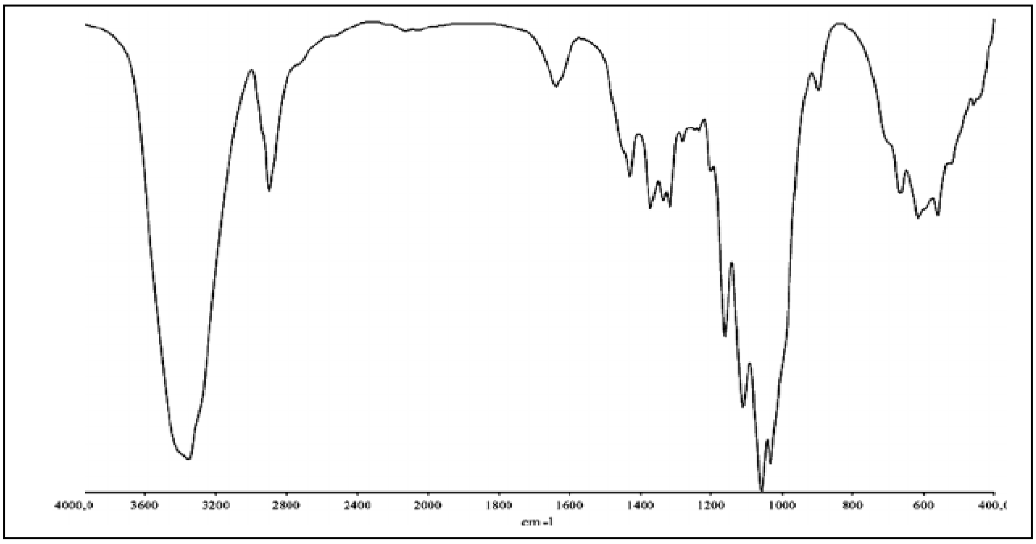
The sample prepared in this work showed a degree of substitution of 1.76 aldehyde group/anhydro glucose repeat unit.

3.1.2 Analysis by FT-IR

The FT-IR figures of the native cellulose is presented in Fig .3.1. The IR figure shows a broad band at 3429 cm^{-1} corresponding to the O-H. The band at 2936 cm^{-1} attributed to the C-H stretching, the band at 1026 cm^{-1} corresponding to C-O-C stretching.

Figure 3.1

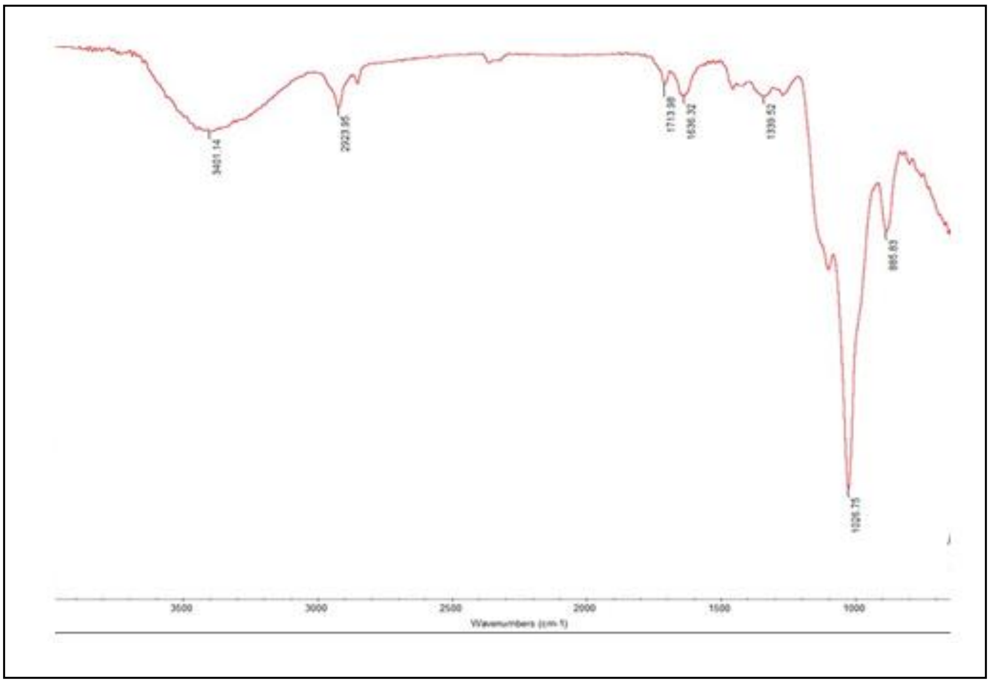
IR spectrum of nanocrystalline cellulose



The recorded IR spectrum of cellulose dialdehyde is presented in Fig. 3.2. The figure shows a band at 1722 which could be attributed to the carbonyl of the aldehyde group. The carbonyl peak appears as a weak band due to hydration and conversion to a hemiacetals.

Figure 3.2

IR spectrum of cellulose aldehyde



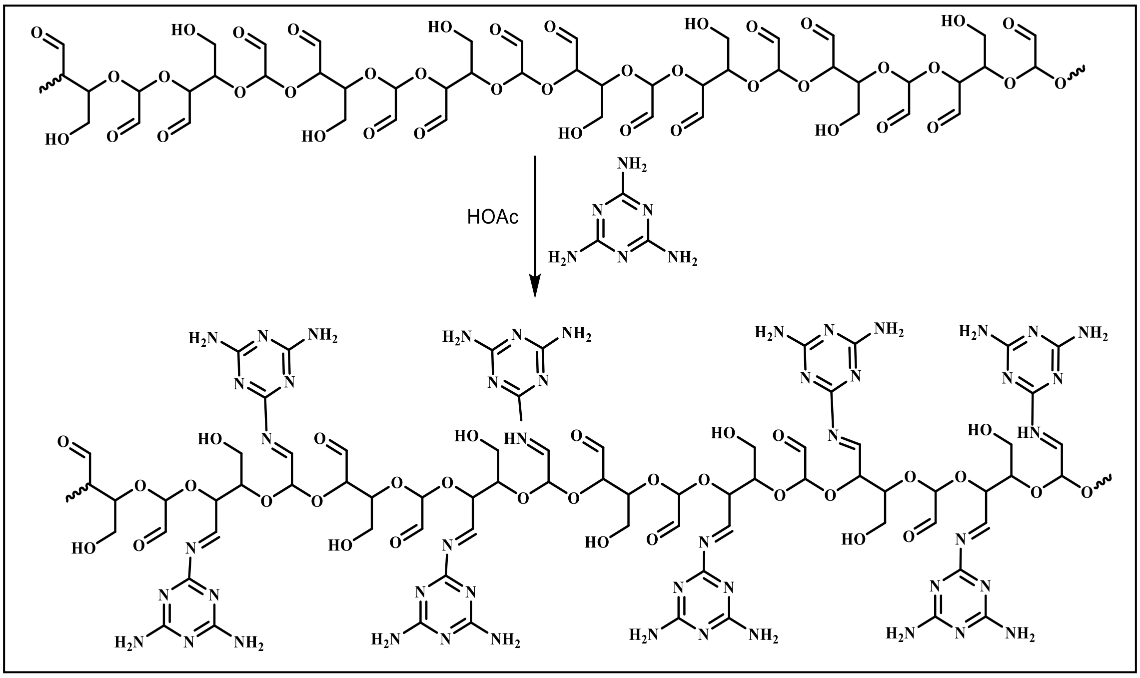
3.2.2 Preparation of cellulose melamine Schiff base

The aldehyde group is reactive and versatile, for this reason it can be used as to prepare other functional groups such as amine, imine, acid, and others.

Cellulose aldehyde prepared previously was derivatized with diimine by reacting it with melamine using methanol as a solvent, acetic acid was used as a catalyst (Scheme 3.3).

Scheme 3.3

Conversion of cellulose dialdehyde to NCC-Mel

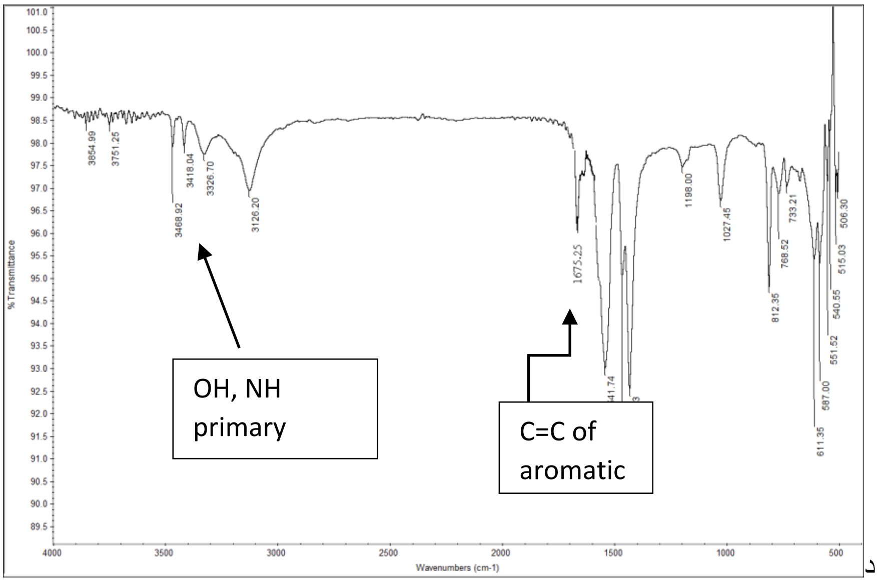


3.2.3 FT-IR analysis of NCC-Mel

The IR spectrum of cellulose melamine polymer shows that the aldehyde group used to show at 1722 cm^{-1} is no longer available and the existence of the C=N at 1675 cm^{-1}, the C=C of the aromatic shows at about 1590 cm^{-1}. The N-H of primary amine and the O-H appear in the range of 3270–3480 cm^{-1} as multiple bands as shown in the figure 3.3.

Figure 3.3

FT-IR spectra of polymer NCC-Mel



3.4 Adsorption results

This adsorption process was performed by nanocrystalline cellulose melamine (NCC-Mel) towards Pb(II) ions. The residual concentrations of Pb(II) were measured using AAS. The % of removal was calculated for each adsorption experiment using Eq. 5. [45]

$$\% \text{ adsorption} = (C_i - C_f) / C_i \times 100\% \qquad \text{Eq.5}$$

Where:

C_i is the Pb(II) Initial concentration in ppm.

C_f is the Pb(II) finial concentrations in ppm.

The adsorption capacity qe (mg per g) was calculated as shown in equation (6) :

$$q_e = (C_i - C_f / m) \times V \qquad \text{Eq.6}$$

Where; V is the volume of solution (L) and m is the mass of the adsorbent in g.

3.4.1 Adsorption of Lead (II) Ions

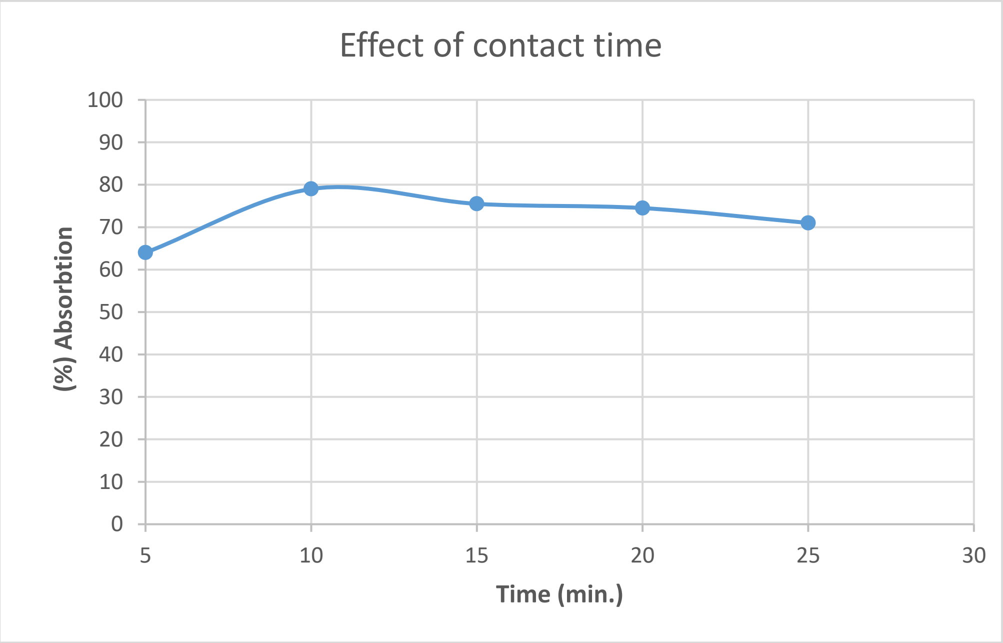
The effect of various parameters on the percentage of the removal of lead(II) ions by the NCC-Mel was evaluated.

3.4.1.1 Contact time

The effect of contact time on the adsorption lead (II) ions by NCC-Mel was evaluated while the other parameters (pH, temperature, adsorbent dose and initial concertation) were kept unchanged, the obtained results are summarized in Figure 3.4.

Figure 3.4

Effect of time on the adsorption of lead (II) by NCC-Me



(Initial conc. = 20.0 ppm, polymer dose = 75 mg, volume of solution = 10 ml, pH was 7 and 25 C).

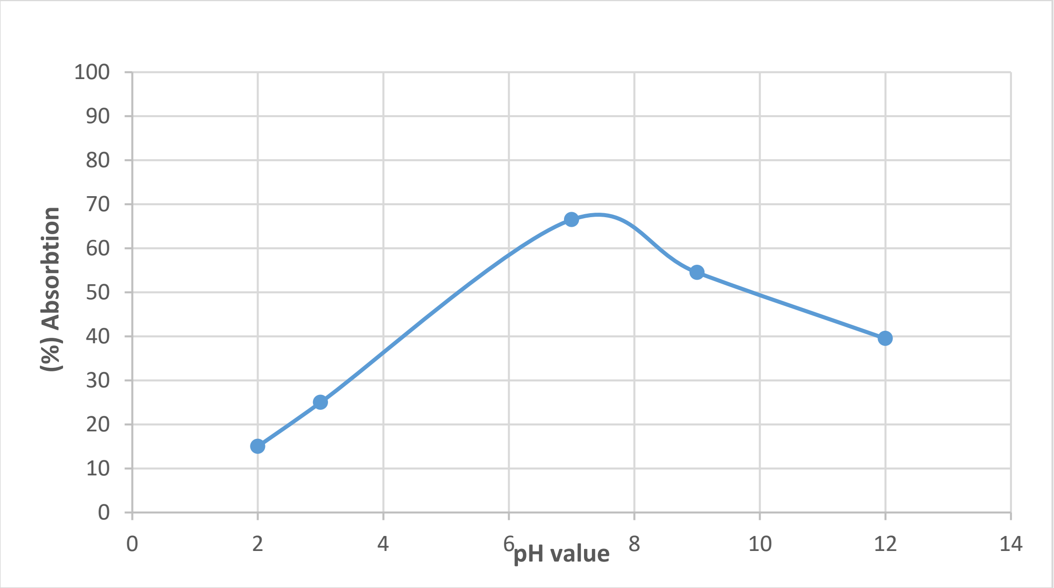
Figure 3.4 shows that the maximum rate of adsorption of lead (II) ions by NCC-Mel occurred at about 10.0 minutes of contact time, the removal efficiency reached about 79%. Then the adsorption became almost constant. The high percent removal of lead (II) ions during initial time could be attributed to the high availability of binding sites then tend to decrease tend to become constant.

3.4.1.2 Effect of pH value

The pH parameter is an important factor in the adsorption process of metal ions since it effects the charges of the polymer functional groups. Figure 3.5 shows the results of the effect of pH value on the adsorption efficiency of NCC-Mel. This study was performed at the determined optimum contact time determined before, while varying the pH of the solution. The other parameters were kept constant.

Figure 3.5

Effect of solution pH on the adsorption efficiency of NCC-Mel)



(Initial conc. = 20 ppm, polymer dose = 75 mg, solution volume = 10 mL, for 10.0 min, T = 22 ºC)

The percentage of Pb (II) removal increased by increasing the pH value, the highest removal attained in the pH rang (6.5-7.5), and started to decline the pH increased. The highest removal of lead (II) was 70.0%., this could be attributed to the lack of competition between the positive metal ions and the protons at the bonding site which will increase the metal bonding.

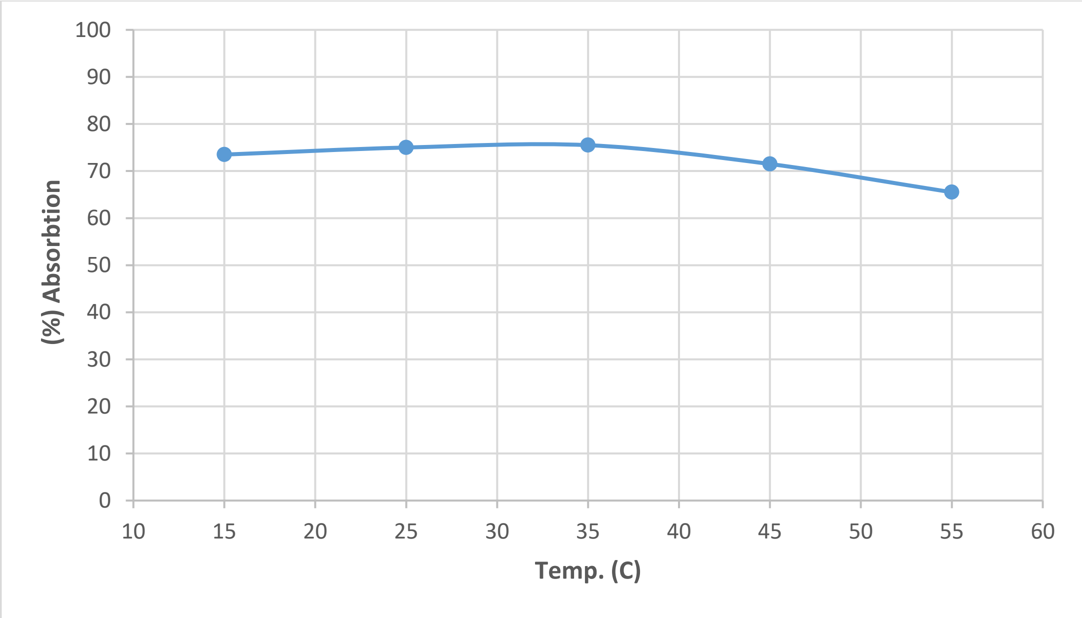
The decrease in the adsorption of the metal ions at low pH could be due to the protonation of amine which decrease its ability to bind to metal ions.

3.4.1.3 Study of temperature parameter

The effect of heat on the adsorption efficiency of NCC-Mel for Pb(II) was also evaluated. The optimum contact time and pH were used in this experiment and the other parameters were kept constant. Results are summarized in figure 3.6.

Figure 3.6

Temperature parameter effect on the removal efficiency of NCC-Mel for Pb(II)



(Initial conc. = 20.0 ppm, polymer dose = 75 mg, solution volume = 10.0 mL, time = 10 min and pH of 7.0)

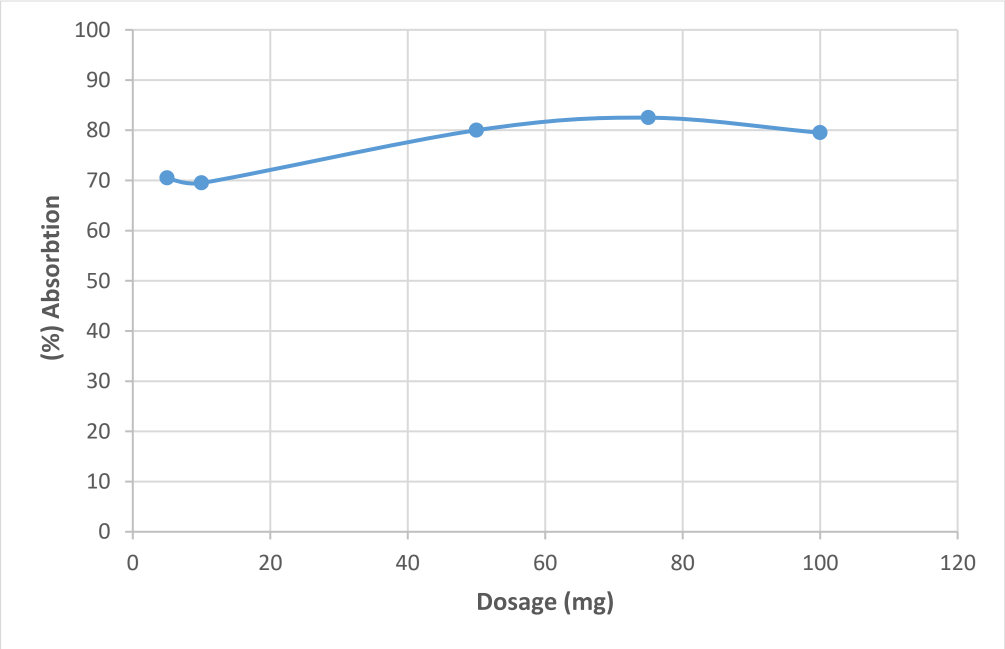
As can be seen form Figure 3.6, the adsorption of lead ions remains constant from room temperature to 35.0 °C then started to decline slightly. The highest percentage of removal 75.0%. The results indicate that the adsorption occurs spontaneously at ambient temperature.

3.4.1.4 Adsorbent dosage

Figure 3.7 shows the results obtained for the removal of lead(II) ions using various amount of NCC-Mel ranging from five mg to a 100.00 mg at the optimal pH, temperature and time.

Figure 3.7

Effect of polymer dosage on the efficiency of lead (II) ions removal



(Initial conc. = 20.0 ppm, solution volume = 10.0 mL, time = 10 min at 25ºC and a pH of 7.0,)

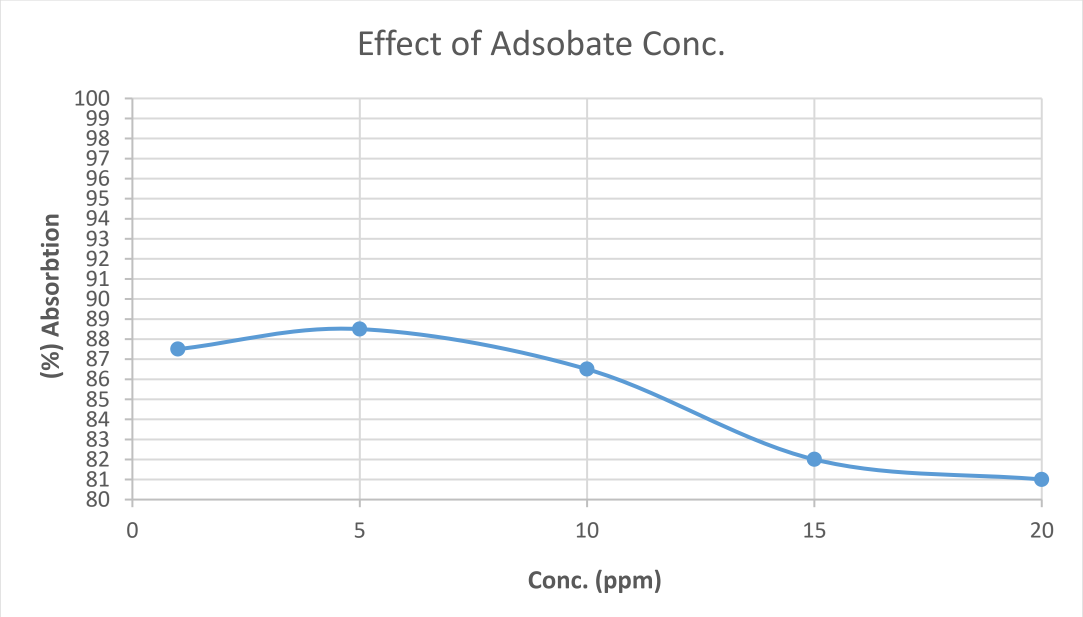
The results shows that the highest efficacy reached using 75.0 mg of NCC-Mel. The removal efficiency increased by increasing the adsorbent dose it 83.0% at 75.0 mg of NCC-Mel. As the amount of adsorbent increases the bonding sites for the metal ions increase.

3.4.1.5 Initial concentration of lead (II) ions

The outcome of the conc. of lead (II) ions on the percentage removal by NCC-Mel is shown in Figure 3.8.

Figure 3.8

Effect of initial conc. of lead (II) on NCC-Mel adsorption efficiency



(polymer dose = 75.0 mg, solution volume = 10.0 mL, time = 10 min, pH value of 7.0, at 35 ℃)

As shown in figure 3.8, the adsorption decreased by increasing the started concentration of Pb(II).The highest adsorption of lead (II) ions was about 88.5% reached at a lead (II) initial concertation of 5 ppm.

Table 3.1

The optimum parameters for the adsorption of lead (II) ions using NCC-Mel

Optimum Condition	Value
Contact Time (minute)	10.0
pH value	7.0
Temperature (°C)	(25.0 -35.0)
Adsorbent Dose (mg)	75.0 in 10 ml solution
Adsorbate Concentration(ppm)	5.0 in 10ml solution

3.5 Adsorption Kinetics

Understanding the mechanism of adsorption is an important factor of discussing the results. So adsorption kinetics was evaluated using the two models pseudo-first and second order (Eq.7 and Eq. 8, respectively) .[46]

$$\text{Ln}\,(qe-qt) = \text{Ln}\,qe - K_1t \qquad \text{Eq. 7}$$

$$t/qt = 1/k_2qe^2 + t/qe \qquad \text{Eq.8}$$

Where;

qe is the adsorbate mass/unit mass of adsorbent at equilibrium (mg/g)

qt is the adsorbate mass/unit mass of adsorbent (mg/g) at time t

K_1: first-rate constant (1/min)

K_2: second-order rate constant (g/ mg min)

3.5.1 Testing the kinetic models on NCC-Mel

In Tables 3.2 and 3.3 as well as Figures 3.9 and 3.10, the results of fitting the lead (II) ion adsorption data by NCC-Mel to pseudo-first and second order laws are displayed.

Table 3.2

Pseudo-first order model results

Time(min.)	ci	cf	qt (mg/g)	ln(qe-qt)
5	20	7.2	1.706666667	-0.791127589
10	20	4.2	2.106666667	-2.931193752
15	20	4.9	2.013333333	-1.919592841
20	20	5.1	1.986666667	-1.752538756
25	20	5.8	1.893333333	-1.32175584

Figure 3.9

Pseudo-first order results

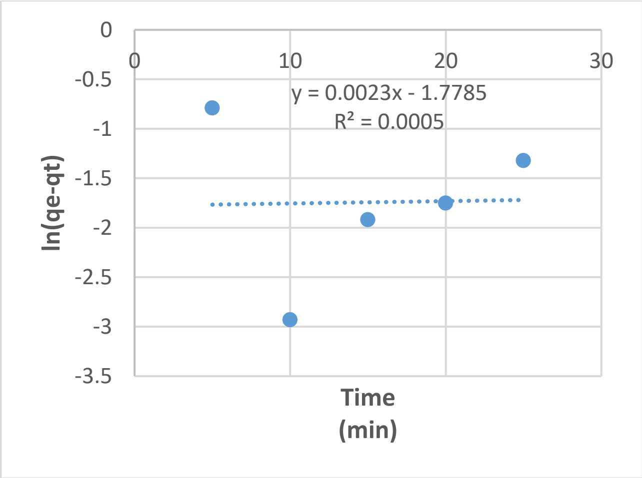


Table 3.3

Pseudo-second order results

time	C_f	qt	t/qt
5	7.2	1.706666667	2.9296875
10	4.2	2.106666667	4.746835443
15	4.9	2.013333333	7.450331126
20	5.1	1.986666667	10.06711409
25	5.8	1.893333333	13.20422535

Table 3.4

Summary of adsorption kinetics

	Adsorption kinetics	
	First order	**Second order**
R^2	0.0005	0.992
Theo. qe	2.16	2.16
Exp. q_e	0.658	1.93
K1	0.0033	_
K2	_	-3.33

Table 3.4 shows that, the correlation coefficients (R^2) for the pseudo 2nd order was higher than that of the pseudo 1st order. R^2 was 0.0005 by first order kinetic and 0.992 by second order, and the calculated q_e value was 2.16. The experimental values of R^2 and q_e values 0.658 and 1.93, respectively were closer to the values obtained by the second order kinetic. This shows that the adsorption mechanism follows the second order rate law.

3.6 Adsorption Isotherms

The efficiency of the synthesized polymer in removing lead (II) ions at equilibrium was studied using Langmuir (Eq.9) and Freundlich(Eq.10) isotherms [47].

If the adsorbate is arranged in a one layer on the polymer surface the Langmuir model (Eq. 9) is applied as shown:

$$1/qe = 1/Qmax\,Klce + 1/Qmax \qquad \text{Eq. 9}$$

C_e : equilibrium concentrations of ions in ppm.

Q: mass of metal ions absorbed/ unit mass of polymer at equilibrium ($mg.g^{-1}$).

Q_{max} is the single layer adsorption capacity of the adsorbent ($mg*g^{-1}$) theoretically.

K_l is the Langmuir affinity constant related to the adsorption energy ($L*mg^{-1}$).

But, if several heterogeneous layers adsorbent and adsorbate are formed, then the process follows the Freundlich model (Eq. 10).

$$\mathrm{Ln}\ qe = \ln k_f + 1/n \ln C_e \qquad \text{Eq.10}$$

K_f is the Freundlich constant related to adsorption capacity ($mg*g^{-1}$).

N is the heterogeneity coefficient ($g*L^{-1}$)

Equation 9 was used to determine if the adsorption process is attractive and favorable or not, this can be done by the determining the value of dimnsionless constant separation factor (R_l) as shown in Eq.11, which is derived from the Langmuir model.

$$Rl = 1/(1+ KlCi)= 1 + 1/ KlCi \qquad \text{Eq.11}$$

Where;

C_i is the initial Pb(II) conc. In ppm.

R_l is the separation factor.

If:

$R_l > 1: adsorption is$ unfavorable

$0 < R_l < 1: adsorption is$ favorable

$R_l = 1$: adsorption is linear

3.6.1 Testing the two models on NCC-Mel

The obtained results of the adsorption of lead (II) ions by the polymer NCC-Mel were fitted in the two isotherm models. The obtained results are shown in Tables 3.5 and Fig.3.11 for Langmuir model and in table 3.6 and Fig.3.1 2for Freundlich model.

Table 3.5

Langmuir model of adsorption of Pb^{2+} on NCC-Mel

Ci	Cf	Qe	1/Ce	1/qe
1	0.9	0.013333333	10	75
5	2.4	0.346666667	0.384615385	2.884615385
10	2.5	1	0.133333333	1
15	3.6	1.52	0.087719298	0.657894737
20	3.8	2.16	0.061728395	0.462962963

Table 3.7 summarizes the obtained values of Freundlich and Langmuir isothermal coefficients for adsorption of Pb (II) ions on the NCC-Mel polymer surface.

3.7 Adsorption thermodynamics

Van't Hoff plot can be used to determine the thermodynamic parameters ΔH and ΔS of the adsorption process. They can be calculated from the slope and the intercept of the graph of Ln_{Kd} versus (1/T) [46].

3.7.1 Thermodynamic parameters

The data obtained from the adsorption of lead (II) ions on NCC-Mel were applied to the thermodynamic equations. The obtained results are shown in table 3.8 and figure 3.13.

(Time = 10.0 min., initial conc. = 20.0 ppm, adsorbent dose = 75 mg, solution volume = 10.0 mL at a pH of 7.0,

The results in the table shows that the adsorption of lead (II) ions on NCC-Mel is an exothermic process (ΔH < 0) and spontaneous (ΔS < 0)

3.8 Metal ion content of the sewage after the purification process

The efficiency of NCC-Mel on adsorption of toxic transition metal ions present in a real sample of wastewater was evaluated.

A sample of sewage was collected and treated with the NCC-Mel polymer. The optimal conditions obtained for this study were considered. The assay was performed at 35 ° C, a pH value of 7, 75.0 mg of polymer, and shaking time of 10 minutes.

The initial and the final concentrations of the toxic metal ions present the sewage sample are summarized in table 3.10. The analysis was carried out using ICP-MS (Water center at An-Najah National University). The polymer showed excellent removal efficiency for most ions present in the sewage sample.

3.9 Conclusion

Nanocrystalline cellulose (NCC) polymer was prepared by hydrolysis of cellulose, which was obtained by an extraction process form the industrial waste of the olive oil pressing. The NCC was oxidized using sodium periodate in a dark environment, obtained degree of substitution equal 1.75 ald per anhydroglucose unit. Oxidized cellulose was reacted with melamine to prepare the nanocrystalline cellulose melamine (NCC-Mel) which carries multiple amine groups. Optimum value of the adsorption parameters temperature, contact time, pH an adsorption dosage was determined. The adsorption rate was close to excellent using the determined optimum parameters. A sample of sewage was obtained from a plant in Palestine from and treated with the NCC-Mel. The ions removal efficiency from the sewage sample was quantitative. Kinetic and thermodynamic analysis results shows the adsorption process is a second order rate and spontaneous at room temperature.

List of Abbreviations

Abbreviation	Meaning
Mel	Melamine
FT-IR	Fourier Transform Infrared
OISW	Waste of Olive Industry
BO	Oxygen Biological
CO	Oxygen Chemical
EPA	Environmental Protection Agency
WHO	World Health Organization
ΔE	Activation Energy
HBB	Hemoglobin Beta
R^2	Correlation coefficient (regression coefficient, fitting coefficient)
NCC	Nanocrystalline Cellulose
3D	Three Dimentional
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICE	Immigration and Customs Enforcement’s
FAAS	Flame Atomic Adsorption Spectrometer
OC	Oxidized Cellulose
Ald	Aldehyde
Conc.	Concentration
C_e	Concentration of metal ions in the sample solution after treatment at equilibrium (mg/L)
C_i	Initial concentration of metal ions in the sample solution (mg/L)
q_e	The mass of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g)
q_t	Amount of adsorbate per unit mass of adsorbent at time t (min)
Qmax	Maximum monolayer adsorption capacity of the adsorbent (mg/g) theoretically
K_1	The pseudo first order rate constant
K_2	The pseudo second order rate constant
K_f	Freundlich constant which is an approximate indicator of adsorption capacity of the sorbent (mg/g $(L/mg)^{1/n}$)
K_l	Langmuir isotherm constant (L/mg)
Kd	The thermodynamic gas constant

$\frac{1}{n}$	Dimensionless Freundlich constant giving an indication of how favorable the adsorption process
R_l	Dimensionless constant separation factor
H	The change in enthalpy
S	The change in entropy
G	The change in Gibbs free energy
R	The universal gas constant
T	The absolute temperature

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Appendix A

Tables

Table 3.6

Freundlich model for adsorption of lead (II) ions by NCC-Mel

Ci	cf	ce	ln Ce	Lnqe
1	0.9	0.1	-2.302585093	-4.317488114
5	2.4	2.6	0.955511445	-1.059391576
10	2.5	7.5	2.014903021	0
15	3.6	11.4	2.433613355	0.418710335
20	3.8	16.2	2.785011242	0.770108222

Table 3.7

Summary of adsorption Isotherms for NCC-Mel

Adsorption Isotherms						
Langmuir				Freundlich		
R^2	Qmax	K_l	R_l	R^2	n	K_f
1	100.0	0.001	0.9	1	1	0.01

Table 3.8

Thermodynamic data for adsorption of lead (II) ions by NCC-Mel

Temp.	c_e	1/T (K-1)	$\ln_{Kd}$
15	5.3	0.003472	-0.994762347
25	5	0.003356	-0.916290732
35	4.9	0.003246	-0.889443482
45	5.7	0.003144	-1.095109658
55	5.4	0.003048	-1.020280445

Table 3.9

The obtained values of the thermodynamic parameters.

Adsorbent	Adsorption Thermodynamics	
	ΔH (kJ)	ΔS (J/K)
NCC-Mel	-1736.5	-13.8

Table 3.10

Concentration of toxic heavy metals before and after purification

metal ions	conc. Befor (ppb)	conc. After (ppb)	Percentage Removals (%)
Al	4680.0	61.558	98.68
B	156.29	0.009	99.99
Cr	523.00	18.90	96.38
Pb	5840.0	1.173	99.97
Mn	167.00	42.87	74.33
Zn	696.00	21.645	96.89
Cu	103.00	6.666	93.53
Fe	8160.0	436.166	94.65
Se	609.00	1.102	99.82
Ni	430.00	7.495	98.26
Ti	0.100	0.00	100
Co	12.50	0.662	94.70

Appendix B

Figures

Figure 3.10

Pseudo-second results

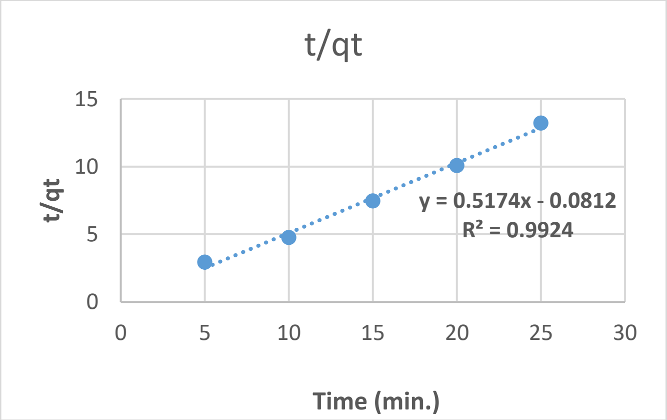


Figure 3.11

Freundlich model plot for adsorption of Pb^{2+} by NCC-Mel

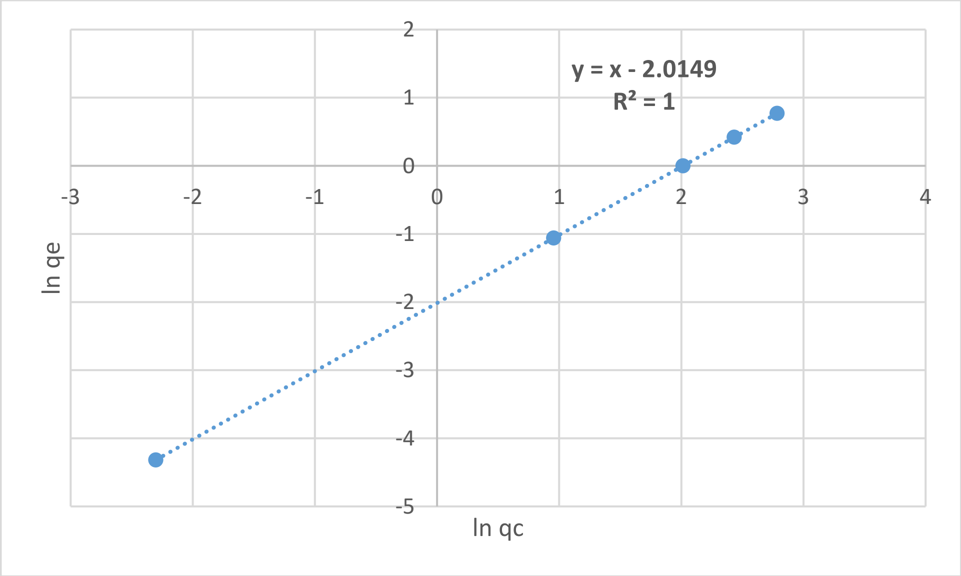


Figure 3.12

Langmuir mode plot of adsorption of lead (II) ions by NCC-Mel.

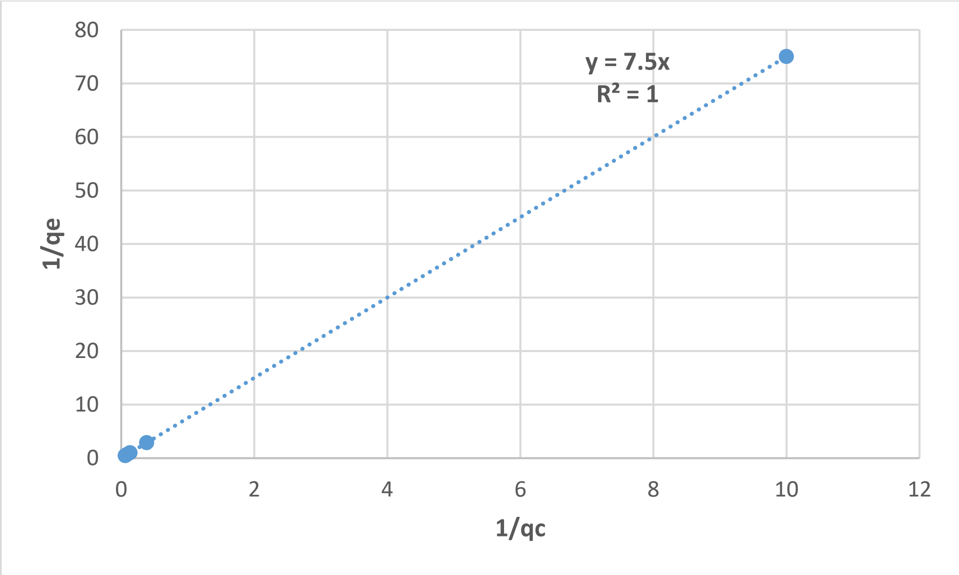
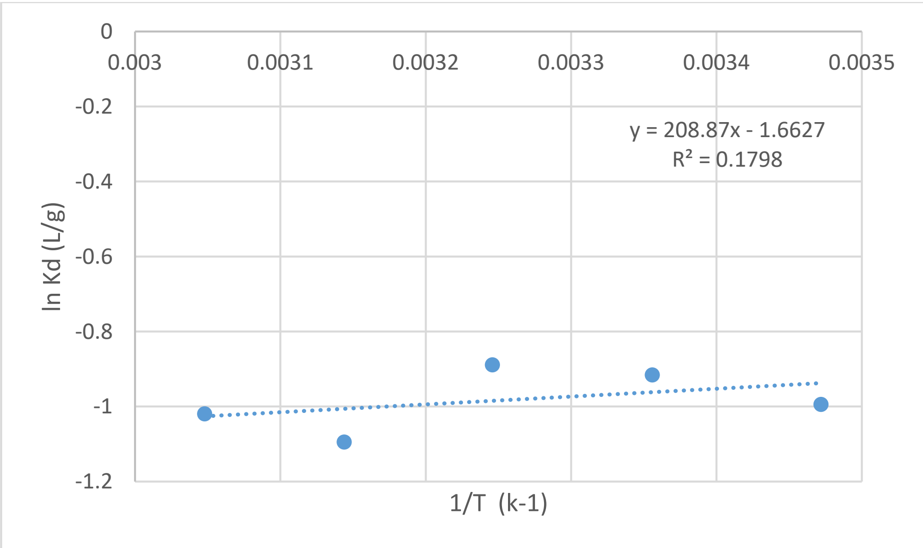


Figure 3.13

Van't Hoff plot



جــامعـــــة النجاح الوطنية

كليـــة الدراســـــات العليــــا

ميلامين السيليلوز البلوري النانوي (قاعدة شيف): التحضير والتطبيق لامتزاز ايونات الرصاص

إعِداد

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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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ميلامين السيليلوز البلوري النانوي (قاعدة شيف): التحضير والتطبيق لامتزاز ايونات الرصاص

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الملخص

الخلفية: في السنوات الأخيرة ، ازداد الطلب على المياه النظيفة لتغطية الحاجة المتزايدة للأنشطة البشرية وإنتاج الغذاء. لذلك ، حظيت المياه الملوثة بالعناصر السامة الثقيلة مؤخرا باهتمام كبير من الباحثين في جميع أنحاء العالم. تميل العديد من الدراسات الحديثة إلى تطوير طرق جديدة لإزالة هذه المواد ، مع الأخذ في الاعتبار أن هذه الطرق يجب أن تكون غير سامة وبأسعار معقولة ، وبالتالي يمكن الاعتماد عليها في تنقية المياه.

الهدف من هذه الدراسة هو استخدام السليلوز كإحدى طرق تنقية المياه العادمة الملوثة بالمعادن الثقيلة السامة.

المنهجية: تتضمن الخطوة الأولى تحويل السليلوز المستخرج من المخلفات الصلبة لصناعة الزيتون (OISW) إلى السليلوز النانوي البلوري (NCC) ، ثم أكسدة السليلوز البلوري النانوي إلى ديالديهيد باستخدام فترة الصوديوم ($NaIO_4$) ، وأخيراً تم تحويل الديالديهيد الذي تم الحصول عليه من الخطوة السابقة إلى imine عن طريق تفاعله مع الميلامين.

النتائج: تم تحليل قاعدة الميلامين السليلوز البلورية النانونية (NCC-Mel) بواسطة FT-IR. تم اختبار كفاءة المحضر (NCC-Mel) كممتاز لأيونات الرصاص (II) الموجودة في مياه الصرف الصحي. تم تقييم وتحسين تأثير جرعة الممتزات ودرجة حموضة المحلول ودرجة حرارة المحلول وتركيز أيونات المعدن

ووقت الخلط. تم عرض أعلى كفاءة تجاه أيونات الرصاص بتركيز 5.0 جزء في المليون من أيونات الرصاص في 10مل من المحلول، و 75.0 مجم من البوليمر في 10مل من المحلول، عند 25.0 درجة مئوية، ودرجة الحموضة7.0 عند التقليب لمدة 10.0 دقائق.

الخلاصة: تم استخدام قوانين الديناميكا الحرارية والدراسات الحركية بحيث أظهرت الحسابات ان استخدام NNCفي إزالة ايونات الرصاص ينطبق عليه قوانين الحركة من الدرجة الثانية. كما ان التفاعل باستخدام هذا البوليمر هو تفاعل طارد للحرارة وتلقائي يمكن الحصول عليه على درجة حرارة الغرفة.

الكلمات المفتاحية تلوث المياه، تنقية المياه، الامنزاز، بوليمر، السليولوز، الرصاص، ميلامين السليولوز البلوري النانوي.