



An-Najah National University
Faculty of Graduate Studies

**CELLULOSE BASED FOAM WITH IONIC
FUNCTIONALITY: SYNTHESIS AND
APPLICATION IN WASTEWATER
PURIFICATION FROM TOXIC METALS**

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Dedication

With genuine gratitude and warm regard, I dedicate this work to my lovely family, people who have faith in me and whose words of encouragement and push never left my side. To whose love for me knew no bounds, to who taught me the values, self-love, and how to appreciate myself and therefore strive for the best that I worth.

To friends and all strangers who made my days with their lovely kind words or behaves, to each smile, word, and even a look.

Also, I dedicate my work to all beauty and love sources blue sky, green spaces, and music that takes me to another era.

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To all supportive people during my journey thank you for being there your presence makes a difference I appreciate your love and help I will not mention a name I will let my words touch your heart.

Declaration

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

CELLULOSE-BASED FOAM WITH IONIC FUNCTIONALITY: SYNTHESIS AND APPLICATION IN WASTEWATER PURIFICATION FROM 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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CELLULOSE-BASED FOAM WITH IONIC FUNCTIONALITY: SYNTHESIS AND APPLICATION IN WASTEWATER PURIFICATION FROM TOXIC METALS

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Abstract

Background: The excessive applications of chemicals increased the load of contaminants in water. Organic, heavy metals ion, and inorganic contaminants pose a serious risk to creatures' life. heavy metal ions are one of the most harmful common contaminants. Scientists devoted their effort to finding an efficient, economic, commercially available, and environmentally friendly way to remove contaminants from water.

Objectives: In this study, we benefit from Polyurethane foam (PUF) characteristics. PUF is easy to prepare and use in water purification. Elastic porous structure, controllable pore structure, adjustable shape, simple preparation process, high stability, and high adsorption/desorption rate. These properties make it very suitable for use as an adsorbent material for toxic metal ions. The lack of metal-binding groups in PUF limited its use in wastewater purification. PUF modified with an ionic functional group that is covalently attached to it will be synthesized and used as a metal adsorbent.

Methodology: PUF preparation was carried out by polymerizing the diisocyanate compound with oxidized cellulose. The first step involved reacting cellulose with sodium periodate to produce dialdehyde cellulose. Produced dialdehyde cellulose was reacted with para-aminobenzoic acid to form a Schiff base. Schiff base was reduced by sodium borohydride to form cellulose amino benzoic acid. At the last step, a diisocyanate compound was added to form a foam with a 3D structure with carboxyl functionality. The presence of the carboxylate and amino benzoic acid groups in addition to the other PUF properties mentioned above makes the target foam novel for wastewater purification. The prepared polymers were characterized by using TGA, and FT-IR. The produced foam was used in extracting metal ions form wastewater. Optimum adsorption conditions for wastewater purification process using the prepared cellulose PUF polymers was detected.

The adsorption conditions that lead to the highest efficacy were determined by running the extraction at various parameters such as: pH, contact time, temperature °C, dosage, and initial metal ion concentration.

Results: The effect of each parameter was evaluated by varying the parameter values while keeping others constant. The targeted parameters that lead to the highest efficacy were determined to be pH 7.0 and 9.0, contact time 30 and 25 min, temperature 15 and 20, dosage 250 mg, and initial metal ion concentration 15.0 and 20.0 ppm for PPUF and HMPUF respectively. An atomic absorption spectroscopy instrument was used to determine the concentration of lead after applying the polymer under certain conditions. After detecting the ideal parameters, the prepared polymers were applied to a real-life sample of wastewater. Under the optimum conditions, the efficiency of the polymers in lead removal was tested. Inductively Coupled Plasma Mass Spectrometer ICP-MS was used to determine the concentration of contaminants in the real-life sample (sewage water) after and before applying the polymer. the Langmuir model was fitted to the equilibrium adsorption data. Van't Hoff plot was used to determine ΔH° (KJ/mol), ΔS° (J/mol.K), and ΔG° (KJ/mol) values they were -7.693, and -31.44, and 9.53, -28.725, -107.2 and 32.44 for PPUF & HMPUF- NCC respectively. The results indicate that the adsorption process is spontaneous at room temperature. Kinetic study showed that the process obeys pseudo second-order the R^2 value for the two polymers are very close to 1.

Conclusion: After detecting the optimum conditions polymers were applied to a real sample and the two polymers show excellent efficiency in the removal of heavy metals.

Keywords: heavy metals, water pollution, cellulose, polyurethane foam, adsorption.

Chapter One

Introduction

1.1 Background

The development in different areas of life, with both positive and negative effects on health, well-being, and socioeconomic aspects presented new challenges to humans. The excessive use of herbicides, pesticides, fertilizers, personal care products, skincare products, pharmaceuticals, and other chemicals poses a serious environmental risk to the ecosystem and human health [1,2]. pollutants mainly include metal ions and organic matters that are released from various sources. Among the toxic heavy metals, ion that raises a serious concern is Pb (II), Cd (II), Hg (II), Cr (II), Ni (II), Zn (II), Cu (II), As (II), and Cd (II) [3]. Heavy metals are toxic, bioaccumulative, and non-degradable which makes them extremely dangerous. There is no safe way to dispose of chemicals released from industrial and human activities which cause water pollution. The wide range of contaminants releasing sources provides us with a large scope of contaminants. Therefore, scientists devoted their effort to finding a safe and economic method to remove these contaminants from water. Several techniques with different costs and effectiveness were proposed. Various methods of metal ion extraction have been used, among these the most widely used are solid-phase extraction, liquid-liquid extraction, and cloud-point extraction or co-precipitation. solid-phase extraction has the advantages of high preconcentration factor, low cost, ease of automation, and usually does not require organic solvents[4,5,6]. Solid-phase extraction is an efficient adsorption method for the removal of toxic compounds from wastewater. The toxic materials are transferred to solid sorbent where they are recovered by elution. The principal goals of solid-phase extraction are trace analytes enrichment and sample clean-up. Solid-phase extraction has been used in many areas, including industrial chemistry, clinical, pharmaceutical, environmental, and food. Various solid-phase extraction formats and sorbents have been developed over time for the process of different sample types and to extend the scope of the method [7]. Solid-phase extraction is not limited to the use of solid particles to extract the solutes from a liquid sample. Air or other gaseous samples can also be passed through a packed tube to extract organic vapors or other substances present in the air sample[8]. Adsorption has been considered one of the best water treatment methods due to its high removal

efficiency without any harmful by-products [9]. Activated carbon (AC) was the first adsorbent material used [10]. The high cost of production and regeneration of AC makes it a bad choice for large-scale water treatment. Drawbacks of AC usage as an adsorbent motivated looking for other alternatives [11]. Cellulose is an attractive alternative that can be derived from natural sources, such as woods, annual plants, microbes, and animals. These include seed fiber (cotton), and wood fibers (hardwoods and softwoods). Abundance, low cost, deriving from a renewable source, and easy to modify chemically make cellulose a promising adsorbent [12]. Heavy metals such as copper ion (Cu (II)) and nickel ion (Ni (II)) causes serious risk to human health it can result in liver failure, headache, neurotoxicity, or even death [13]. Cellulose is reported in the literature as an adsorbent used to get rid of many contaminants due to the advantages of biodegradability and reusability.

The carboxymethylated cellulose fiber (CMCF), a carboxyl methylcellulose (cellulose derivative) application Sim et al. (2014), cellulose-based wastes, banana, and orange peels for removal of various dyes [14] were reported as adsorbents. Removal of heavy metals by using cellulose also was reported. The removal of arsenic by using cellulose nanoparticles [15], cellulose graft copolymers for removal of Pb²⁺, Cu²⁺, and Cd²⁺ ions [16], and cellulose from waste natural material were reported. Cellulosic-based adsorbents especially those obtained from waste such as Kenaf [17], cotton linters [18], wheat straw [17] wood sawdust [20], and rice husk [21] were already investigated as adsorption of various metal ions. Among the other evaluated adsorbents is polyurethane foam (PUF). PUF and derivatives have been studied as a solid sorbent for a wide variety of compounds in different media and for different purposes [22]. PUF has the characteristics of elastic porous structure, controllable pore structure, adjustable shape, simple preparation process, high stability, and high adsorption/desorption rate; it is also easy to separate and reuse, which makes it very suitable for use as adsorption materials. Recently, PUF has been widely used in the preconcentration/removal of metal ions. Some PUF showed excellent adsorbent properties due to their high surface area, [23], resistance to pH changes, low cost, and good stability in organic and aqueous solvents [24]. Moreover, PUFs can be used in batch techniques, column techniques offline, or flow injection with a low resistance to the passage of fluids as happens with other sorbents [25]. Blank PUF has a limited ability to absorb metal ions and organic compounds, and it also suffered from low adsorption capacity and poor selectivity. Whereas the modified

PUF adsorbents such as physically loaded, chemically modified and composite possess highly improved adsorption properties and selectivity which can realize the adsorption and separation of different metal ions from water [26]. In a published work, PUF was utilized to immobilize, carboxymethylated cellulose nanofibrils (CMCNFs), and produced composite was used in industrial water purification, such as its agglomeration, difficulties in the separation from effluent, and regeneration. The composite foams exhibited well-dispersed CMCNFs in Polyurethane (PU) matrices with open-pore structure; the hydrogen bonds result in the enhancement of mechanical strength, which is another requirement of ideal adsorbents for wastewater treatment. The composite foams show high adsorption capacity and the potential for recyclability [27]. In this project the disadvantages present in PUF reported in the literature as an adsorbent for metal ions will be overcome by preparing cellulose-based polyurethane foam with ionic functional that is covalently attached to it.

1.2 water pollution and challenges in water sector Palestine

Palestine is an occupied country faces challenges and many difficulties. Water sector in Palestine is highly affected by the occupation practices. Oslo agreement terms give the occupation access to 80% of water in west bank. Occupation policies aren't fair and the Palestinian can't benefit from the exist water in their land. Water sector in Palestine severe from serious problems these problems aren't in supply only but also the quality. Due to water issues in Palestine there are a serious effort to deal with the quality of the water.

1.3 water pollutants

Water is life and it's a vital matter in human and other creature's life. Problems in water sector have a significant impact in our life and all other life sectors. Many studies were conducted to study the water aspects and evaluate if its valued for human activities and ecosystem or not. Water in nature contain many partials and elements but these should not reach threshold value. Water can contain many elements to a certain limit then it considered polluted water [28]. There are many pollutants occurs naturally such as nitrogen compound, heavy metals, hydrocarbons and radioactive elements [29]. Some pollutants released from industrial and agricultural activities. Agrochemicals, pesticide, surfactants, plastic, and petrochemicals create serious environmental problems and release dangerous contaminants. Source of pollution could be direct or indirect. In direct

sources the contaminant release directly to the water source and this very dangerous and cause death and serious problems do exist life in this area. Indirect sources aren't mixed with water directly but end up there such as leachate comes from the contaminated soil [30]. Human should take care and responsibility to safe water from contamination because he is the primarily affected creature. Get rid of chemicals and any other biological contaminants should be in safe way. Avoiding water from mixing with contaminants and avoiding contamination in surface areas where water exist are very important. Pollutants derive from many sources and it can transfer from one reservoir to another via the water cycle.

1.4 Heavy metals

Heavy metals have nonbiodegradable aspects which makes it a serious risk on human health. Presence of heavy metals in high percent in soil, water and air are very dangerous because it will end up cumulated in human cells and causes serious health issues. Kidney damage, cancer, anemia, hepatitis, miscarriages, encephalopathy, and nephritic syndrome are health issues caused by heavy metals [31-34]. Each metal released from different sources. Lead released from metal mining, polishing, lead acid batteries, and glass paper. Fabric factories, electroplating, photovoltaic cells are the main sources of Cadmium metal [35]. Nickel presence in jewelry, watches and coins causes skin diseases. Wide range of releasing sources, symptoms and diseases caused by heavy metal make it serious concern to humans [36,37]. Many techniques were proposed to get rid of heavy metals such as chemical precipitation, ion exchange, ultrafiltration, reverse osmosis, nanofiltration, coagulation, flocculation, flotation. The previous techniques have limitations as low efficiency and high cost. Adsorption technique surpass all other techniques with its outstanding aspects. Many adsorbents are available in nature such as clay, zeolites, red mud, and chitosan. Adsorbents use for heavy metal removal have high efficiency, easy technique to use, low cost, easy to recover, collect and regenerate [38]. The commercially used adsorbent that were reported carbon nanotubes, activated carbon and graphene. Natural materials are cheaper, available and have a high tendency to modification of the surface to increase the adsorptive activity. Bio adsorbents also used for heavy metal adsorption via binding the metal ion functional group on the adsorbent surface such as fungal biomass [39], bacterial biomass [40] peat [41] and others. Some of agricultural, industrial and animal waste can be used as adsorbents for heavy metal removal these

sources are abundant low cost and solve disposal problem of these wastes. Agricultural wastes contain cellulose, hemi cellulose, sugar, starch and lignin it can be used instead of activated carbon it is less efficient but abundant and has very low cost. Wastes adsorbents mostly contain functional groups that increase the efficiency of adsorption such as aldehyde, amine and ketone groups. Functional groups work as binding sites for heavy metal ions. In addition to the presence groups the surface can be functionalized with other groups. Orange peels, nut shells, rice husk, sawdust, and wheat straw are wastes can be treated and used as an adsorbent [42]. Chicken feathers, egg shell, fish scales and crab shell particles are examples of animal wastes [43-46]. Fly ash that produced from coal one of the industrial wastes used as an adsorbent [47].

1.5 lead

World health organization reported many facts about lead poisoning which poses a serious issue for human health. Lead is a cumulative metal effect on human body systems. The brain, kidneys, bones, and liver are the most affected by lead accumulation. Children poisoned by lead sever from many risky symptoms antisocial behavior, lower intelligence quotient (IQ), abnormal brain development, a disorder in the central nervous system, coma, and even death. Lead can be found in paints, leaded fuel, cosmetics, Acid batteries, some medicines, and other sources [48-50]. Due to the dangerous risk of lead, there is a global tendency to reduce the use of leaded products. The Environmental Protection Agency (EPA) reported the limit of Pb^{+2} concentration in drinking water to be less than 15 ppb. Many methods were used to determine lead contamination in water such as atomic absorption spectroscopy and inductively coupled plasma spectroscopy [50]. In palestine there are special sources of lead and other heavy metals due to use materials doesn't meet with the health concern and the allowable limits. In 2019 a study were conducted to study the quality check of herbs products that widely used in palestine. The study shows that herbal medicines used in palestine doesn't meet with the health requirments[51]. In 2017 levels of cadmium, lead and arsenic were determine in humam milk. The study cases were selected from jenin. The study shows that the human milk contaminated with lead and other heavy metals in different degrees. The women live in industrial areas or ares with agricultural activities and waste disposable sites are find to have higher degree of contaminants in breast milk. From the previous study we can conclude that the precense in places full of contamination sources will rise the exposure to the contaminants.

Pollutants reach to human body from plants and water they eats and drinks. Industrial and agricultural places are contaminated environments shows high pollution degress such areas suffer from soil and water pollution[52]. One of the most known sources of water in Palestine is rainwater harvesting. Many samples from households in hebron was collected to study the percentage of heavy metal exist in these samples[53]. The percentage of lead and other heavy metals were exessed the limits. The main cause for the contamination is the circumstances on the surface area surrounding the well. Munciple solid waste was reported as a main source for Pb. Metallic roofs, metal pipes and storage tanks also reported as source of Pb [54-57].

1.6 Adsorption technique

Adsorption technique was used since ancient time it was embodied in many phenomena. Since decades solid was used to remove dyes from solution and purify air from unpleasant odours by using charcoal. Such phenomena known but can't be understood until recent time. Adsorption term become known and used in twentieth century. Scientists attempt to understand and shed the light on the adsorption technique core. In simple words and as it first interpreted the adsorption based on interaction between the adsorbent surface and molecules (physical interaction between the pours and molecule). Adsorbent industry starts from charcoal it was firstly used in gas masks and decolouring of liquids. Clay and carbon were one of the most ancient adsorbent. The most important aspects in the required adsorbent were reported as having high porous surface with large internal volume, strength, resistance and good kinetic and thermal properties. One of the most properties that should take in consideration the applicability of the adsorbent to regenerate without damaging the active sites and lost the adsorptive properties. After discovering and understanding the core of adsorption process it become widely used for recovery of large scope of particles at certain medium. Adsorption used as a pre concentration technique to collect any traces in certain medium and apply it to instrument for testing. The new track in chemical analysis focused on using instrument for the analysis. Using instruments give us many advantages such as speed, reproducibility and accurate determination. The most commonly and popular instruments are that used instruments provide separation through chromatographic techniques and detect using spectroscopic techniques. High-performance Liquid Chromatography (HPLC) and Gas Chromatography (GC), coupled with various detection units. Most sample cannot introduce directly into instrument, the

analyte should have certain concentration limit to be detected. Before introduce samples to the HPLC instrument samples should pass through stage called sample preparation this pre-treatment depends on the analyte nature to make it suitable for applying to the instrument for detecting. interference between analyte and other contaminants in the matrix required isolation (Extraction) to reduce the effect of other contaminants. Concentration level of analyte should have a limit so preconcentration treatment should done in order to enrich the analyte to be detectable. The most common sample preparation is Extraction the separation of compounds based on the difference in solubility of compound in two immiscible phases To understand the principles of extraction and the factor affects the efficiency of separation the distribution should be understood there is two common type of distribution the partitioning when the solute distribute it self between two immiscible liquid phases or adsorption when the solute distribute itself from liquid phase to solid surface and this distribution is dynamic equilibrium it affected by the temperature and other common factor affect the extraction the vapor pressure , solubility, molecular weight hydrophobicity and acid dissociation. The most common extraction techniques is liquid-liquid Extraction (LLE) are consumes a lot of time, tedious, economically and environmentally not favorable, due to use of large quantities of solvents So to avoid the large use the solid phase extraction (SPE) or Liquid-Solid extraction (LSE) utilize solid surface as adsorbent phase which the compound retained on the solid phase that the analyte have greater affinity to it and this compound can be back-extracted by eluting with a desorption solvent with a greater affinity for the analyte after the separation of solid phase by filtration or centrifugation in order to make the method more simple and fast by using magnetizable adsorbent which can be isolated from the sample matrix via an external magnet this evolution of SPE called magnetic solid-phase extraction (MSPE) so the conventional techniques are not effective the new trend in sample preparation that agree with green chemistry and the aim of the sample preparation to isolate the analyte in few microliter and pre concentrated in order to avoid the interference between analyte and other compounds I.E. to eliminate the sample matrix complexity. Accumulation of sorbet on adsorbent surface completed by interaction between the surface and particles. Dipole, induced dipole, electrostatic attraction and van der waals forces causes the interaction [58]. Adsorption can be used to recover gases and solid at large scale and even tiny amount of particles. This study focus on using adsorption technique to extract heavy metals from water. Water contaminated by chemicals that

release organic and inorganic pollutants. Scientists devoted efforts to get rid of contaminant in safe efficient ways. Organic contaminants can be reduced to CO₂ and water with no harmful byproduct. Semiconductor nanotechnology was used to get rid of organic contaminants. Semiconductors works as photo catalyst causes photo degradation of organic contaminants. Photodegradation represent a great choice for water purification process due to the complete mineralization of the contaminants with no byproduct. For photodegradation process low-cost, abundant, stable, non-hazardous semiconductors are used as photocatalysts such as ZnO, & TiO₂. Photodegradation process based on using photocatalyst (semiconductor) for degradation of organic contaminants under light radiations. Semiconductors have the ability to convert water to hydroxyl radical in presence of light. When SC absorb light electrons get energy from the sun light photons. Each band of photons has a different amount of energy. If there is a matching between photon energy and band gap energy, electrons can be moved from valance band to conduction band, free electrons will yield. The first step in photo degradation process is activation of the semiconductor, the hole that form as a result of excitation oxidized water by forming OH radical, then the electron in the conduction band reduce the oxygen to form superoxide anion, Super oxide can react with water to form OH radical again. Hydroxyl radical easily oxidize an organic species to CO₂, H₂O and other less hazardous minerals. Although photo degradation is a great choice researchers face challenges through their work. Some photo catalysts are not easy to recover after finishing the catalytic experiments such as TiO₂. Using supporting material such as activated carbon, sand, Kaolin and other substrates will make recovery process easier. In addition to facilitating recovery process using supporting material will provide us with another aspect such as increasing surface area for contaminants & catalyst interaction which will enhance the efficiency. Another problem is that some of used SC absorb light in the UV region which represent only 4-5% of the solar radiation. Sensitization will solve the problem by effecting on the band gap energy and effectively sensitizes SC to visible region. Some sensitizer such as CdS and Ru dyes cause serious problem due to leaching out hazardous material (heavy metals). Natural dyes such as curcumin & anthocyanin represent safer promising & commercially available dyes. The main sources of organic contaminants are pharmaceuticals, skin care product, personal care products and organic dyes. in such studies of photo degradation, they aim to prepare the catalytic system that give higher efficiency as much as possible and optimize the reaction condition or

parameters to enhance the efficiency. After catalytic system preparation photo catalytic experiments & control experiments will be Conduct. Usually experiments conduct by adding water contain the contaminant particle to the catalytic system in presence of light source such as halogen spot lamp, Xe lamp or direct solar light. The reaction followed by syringing out small aliquots of reaction mixture at different times to determine contaminant concentration. The reaction followed by syringing out small aliquots of reaction mixture at different times to determine contaminant concentration at certain times. Control experiments conduct many times each time they release one of the reaction effective element to insure the importance of these elements. Experiments conduct in the dark to check the amount of adsorbed contaminants on the catalyst surface and to verify the importance of presence of light. Conduct experiments in absence of catalyst to check if there is any loss of contaminants with no catalyst. Use cut off filter to confirmed the ability of sensitizer to sensitize the SC. Through the catalytic experiments many factors will be studied such as effect of PH, Effect of contaminant concentration, effect of temperature and effect of catalyst concentration by conducting experiments under different values of these parameters. There are many devices are used for characterization of catalyst surface and determine different concentrations. Spectrophotometer used to determine concentrations at specific maximum wave length for each compound. Polarography used for detect the ions such as Cd^{2+} and Zn^{2+} . XRD technique is used for characterization of nanoparticles surface and determine the particle size. SEM is used to study surface morphology. Both XRD & SEM used to determine surface structure, morphology and determine Nano particles size. Energy dispersive X-ray (EDX) used to determine atomic ratio and mass ratio between atoms in the compound or catalytic system. Thermo gravimetric analysis (TGA) used to determine the mass ratio in the composite catalyst. Perkin-Elmer LS50 Luminescence Spectrophotometers Photo luminescence (PL) spectra used to detect the desired material by measuring spectra for the presence material and compare it with other spectra in literature to identify the catalyst. Solid electronic absorption spectrum used to measure the absorption spectrum for the catalyst so we can confirm the nature of the catalyst, each absorption spectrum related to specific catalytic material. UV-1601 spectrophotometers which measure the absorbance at a particular wavelength. power X-ray diffraction (XRD) also used for phase identification of a crystalline material and can provide information on unit cell dimensions, diffuse reflectance spectroscopy (DRS) for the optical properties. TEM also

used for characterization of surface morphology. Materials & methods used to do such experiments we should have the material needed for the catalytic experiments. Methyl orange is one of the organic contaminants that was treated by photo degradation process. Many catalytic systems were used for degradation of methyl orange. Silica/TiO₂ /CdS systems, AC/ TiO₂ /anthocyanin system and AC/TiO₂ /Curcumin catalyst systems for these experiments we need material for catalyst preparation TiO₂ , AC, sensitizer (anthocyanin, Curcumin & CdS) and the contaminants (methyl orange). For all catalytic experiments we need material for catalytic system preparation (photo catalyst, supporting material & sensitizer) and we need the contaminant. phenazopyridine in water degraded by these catalytic system sand/TiO₂ /CdS system and AC/ZnO, curcumin (a natural dye) sensitized TiO₂ (anatase) nanoparticles. All the previous catalytic system in addition to polypyrrole grafted ZnO/chitosan (Ppy/C/Z), Graphene oxide (rGO) supported polypyrrole/CdS nanocomposite, Zinc oxide (ZnO) nano-particles were chemically deposited onto montmorillonite (MONT) clay particles, and other system are used for photo degradation of many organic contaminants. Some of these catalytic system used for killing and complete mineralization of two gram negative bacteria in presence of light. photo degradation is a promising technique for water purification. Using supporting material and sensitizer will enhance the efficiency and solve the problems that face the researchers. Also optimization of the reaction conditions and parameters will enhance the efficiency. The wide range of possibilities and factors that we can work on to adjust the catalytic system and enhance the efficiency make photo degradation process scalable [59-61]. In 1972 TiO₂ photocatalytic activity was reported and this highlighted the importance for metal oxides catalytic activity [62]. Degradation principle based on benefiting from electron- hole pair phenomena to produce active radical such as hydroxyl radical that degrade organic compounds. Inorganic compound can't be degraded as organic compound so scientists find other way to get rid of inorganic matters exist in water. Among the several used and proposed techniques adsorption is considered one of the most useful and efficient removal techniques of the contaminants. Adsorption can be used for organic and inorganic contaminants even in low concentrations. Many factors controlled the efficiency of the adsorption process including the adsorption process conditions and the chemical and structure nature of the sorbent. The adsorption performance mainly depended on the interaction between sorbent and sorbate. There are different types of sorbent based on which contaminants need be removed: specific contaminants absorb one

specific contaminant in the sample, selective sorbent removes two or more contaminants, and general sorbent removes many contaminants. Carbon nanotubes activated carbon, and cellulose are considered one of the general sorbents. In recent years, many sorbents were reported for heavy metal removal especially lead. The researchers devoted their effort to enhance the adsorption efficiency of the commonly used adsorbent. Functionalization of the adsorbent surface increases the efficiency and gives the opportunity to create unique outstanding sorbents. Synthesis and functionalization of carbon-based nanomaterials, modified biochar, combination of iron nanoparticles and cellulose nanofibers obtained from Moringa, magnetic carboxylic functionalized CNC (MCNC-DPTA), and many other examples of surface-modified adsorbents were reported for lead removal [63-66].

1.7 Types of adsorbents

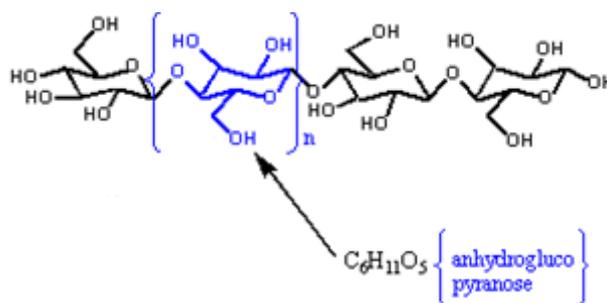
Adsorbent can be classified as synthetic, semi synthetic and natural adsorbents. Synthetic adsorbent is the most expensive one with high adsorptive efficiency while the natural adsorbents is abundant, low cost and environmental friendly but less efficient. Semi synthetic adsorbents its natural adsorbent with chemical modification its cheaper than synthetic one and more efficient than natural adsorbent. If we want to categorize the adsorbents due to adsorption type it classified to chemical and physical adsorbents. This kind of categories relate to the bonding force between the adsorbent and adsorbate.

1.8 Cellulose

Cellulose discovered by agricultural French chemist he noticed that all plants contain fibers with uniform structure. Cellulose is a cheap biodegradable natural polymer that can be extracted from different parts of the plant. Cellulose is a polymer material with the monomer D-glucose repeat unit that is bonded successively through β -1,4-glycosidic joints in the β -configuration between carbon 1 and carbon 4 of adjacent units to form a polymeric chain (Scheme 1.1).

Scheme 1. 1

Cellulose structure



Each D-anhydrous glucopyranose unit possesses three hydroxyl groups two secondary at C2, C3, and one primary at C6 positions. Cellulose is present in form of chains held in as layers by strong hydrogen intermolecular forces. The presence of 3 hydroxyl group for each monomer provide strong intramolecular hydrogen bonds. The presence of inter and intra forces give cellulose structure rigidity and stability. The hydroxyl groups are capable of reacting like small molecules with primary and secondary alcohols. Cellulose has been an industrial feedstock for a large number of industrial products and is also used as a source for bioethanol. Surface modification of cellulose is of great interest due to a wide range of potential applications in food, medicine, cosmetics, LCD films, and many others [67]. Cellulose-based bio adsorbent is a promising choice for the heavy metal extraction process due to its characteristics large surface area, stability in different solvents, great adsorption/ desorption rate, and rapid kinetics. In the last years, large volumes of cellulose originating from agricultural or industrial activities was produced as cellulosic waste material. Recycling and using the cellulosic waste as sorbent could provide us with an innovative solution to the waste problem as well as a useful material. Natural cellulose has some drawbacks, so researchers tend to deal with the modified one. Olive trees form an authentic part of Palestinian history; a huge amount of olive solid waste is produced per year. Extracting cellulose from the olive industry solid waste (OISW) helps in solving the serious disposable problem. Instead of leaving left to rot or burn and release CO_2 into the atmosphere it can utilize and convert into useful and low-cost marketable products. Cellulose modification initiated from hydroxyl group functionalization. Cellulose ester and ether are the most common cellulose derivatives[68,69]. Cellulose also can be oxidized to get carboxylic acid or aldehyde functional groups[70]. One of the most used cellulose modified intermediates CMC. CMC has high viscosity and is nontoxic. So, it mainly used in food as a viscosity modifier or thickener, and to stabilize emulsions in

various products including ice cream. It is also a constituent of many non-food products, such as toothpaste, laxatives, diet pills, water-based paints, detergents, textile sizing, reusable heat packs, and various paper products. CMC is used as a lubricant in artificial tears. CMC can be prepared via reacting cellulose extracted with sodium hydroxide. Sodium hydroxide abstracts an acidic hydroxyl proton of the cellulose chain and converts it into cellulose alkoxide, which is a highly reactive intermediate. This step is common for the preparation of cellulose ethers. Produced cellulose alkoxide then will be reacted with chloroacetic acid. The degree of substitution usually doesn't exceed 0.8 to 1.2 carboxyl groups/repeat unit. Non modified cellulose have a low efficiency in heavy metal adsorption and have less advantages than modified one. Modified cellulose have higher efficiency, stability, good physical and chemical aspects. Ion exchange capability, resistance, elastic and hydrophilic properties all these affected by chemical modification. Esterification, halogenation, etherification and oxidation are the most known modification process. Esterification can be done by using citric acid which react with hydroxyl groups to form ester linkage [71]. Esterification increase the carboxylic content which work as an active site for heavy metal as reported in literature the adsorption tendency was increased [72].

1.9 Cellulose Dialdehyde

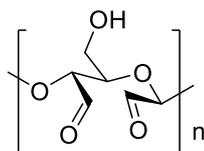
Functionalization of cellulose and surface modification enhances the activity of cellulose. Oxidation of cellulose is a conventional modification method and it destroys the cellulose structure. Dialdehyde cellulose is considered one of the most attractive intermediates for cellulose functionalization. The most common oxidation process of cellulose used is by using periodate. Periodate oxidizes cellulose via selective cleavage of vicinal diols. Carbonyl structure formed on C2 and C3 positions. CDA can be converted to other functionalities such as carboxylic acid, sulfonic acid, and amino acids also it can be converted to Schiff base by reacting with a primary amine [73].

The produced functionalities act as chelating groups on the cellulose surface and form active

sites for metal ions removal [74]. CDA (scheme 1.2) was reported as intermediate for many functionalities in literature such as Cellulose Schiff Base as a Bio-based Polymer, CDA used as chemisorption adsorbent [75, 76].

Scheme 1.2

Chemical structure of cellulose dialdehyde

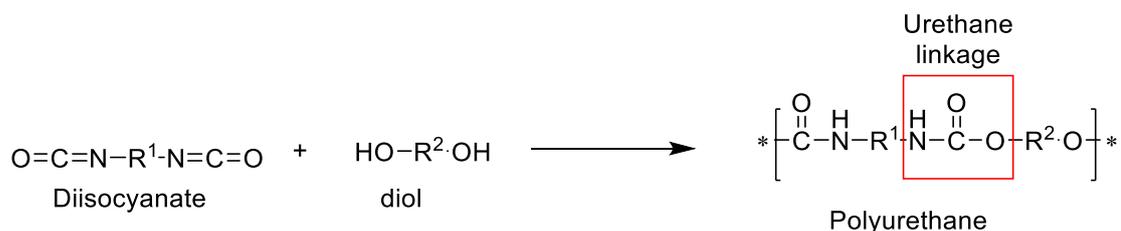


1.10 Polyurethane Foam

PUF is a polymer containing urethane linkage it was reported for the first time in 1937 [77]. PUF was discovered while the researchers were working on plastic products. The foam structure could be flexible, semi-flexible, and rigid due to the preparation process that can produce open or closed cells foam structure[78]. PUF is widely used in many sectors as construction, building, and electronics. In modern countries, PUF wastes are produced in huge amounts so the need to recycle them reuse them is very important. PUF was reported as an oil adsorbent, in constructions and as an adsorbent for wastewater pollutants. PUF is an outstanding adsorbent can be used other than many expensive and less efficient adsorbents. Open cell structure of PU and the aspects of surface with many pores shed the light toward PU as an adsorbent. PUF in end of life refrigerators was reported as an adsorbent for wastewater treatment [79-82]. The versatility of PUF comes from the wide range of polyols and isocyanate that can be used in PU synthesis. Polyurethane foams are usually prepared from polyesters and polyether. One of the most known preparation techniques is by using isocyanate by polycondensation reaction between diol and diisocyanate. This reaction may be required presence of a catalyst and other additives. The general reaction is shown in scheme 1.3.

scheme 1.3

Polycondensation reaction



The diisocyanate suitable for use could be aliphatic or aromatic ones. Aromatic isocyanate is more reactive than aliphatic due to the resonance structure and charge distribution throughout. The presence of the R withdrawing group enhances the activity of the isocyanate toward the nucleophilic attack of the aromatic ring. The isocyanate can react with all active hydrogen (OH, H₂O, and NH) Isocyanate is very toxic and causes serious concern to human health [83]. Elastic, resistance to oxidation, stability, and strength all these are aspects that controlled by preparation method of PU. The polyols and diols chain length control the flexibility and rigidity of the PUF. Isocyanate used in preparation is short chain and it is responsible on the hardness of the PU. PU undergo many additive process to increase its applicability to use as adsorbent. To improve the adsorption capacity of PU, increase the hydrophobicity, surface area, selectivity, hydrogen bonding, ionic bonding and ion- dipole interaction were suggested and reported in literature [84,85]. The major factor in chemical modification of PU is the chains in the foam matrix. A cellulose acetate–polyurethane (CA–PU) film adsorbent, polyurethane foam (PUF), and many other PUF were reported as the lead adsorbent [86, 87].

1.11 literature review

As reported in recent works researches adsorption technique still considered the most attractive technique for heavy metal removal. The future adsorbents that reported in literature and scientist focus in are adsorbent from wastes. Adsorbents prepared from wastes solve waste disposal global problem. A novel adsorbent was reported nanoadsorbents including graphene, graphitic carbon nitride (g-C₃N₄), MXenes and metal organic framework (MOF). These adsorbents reported with unique physical and chemical properties which makes it a promising adsorbents [88]. Industrial solid wastes were reported as adsorbent for heavy metals. Organic and inorganic solid wastes as construction, mining, food and others industries were reported [89]. Brewed tea wastes

one of the adsorbents used for wastewater treatment its reported as one of the low cost eco- friendly adsorbents the adsorbent was prepared and characterize then batch experiments conducted to study the adsorption optimum conditions and the data applied to isotherm models to make isothermal study [90]. Natural- aged micro plastic was used to capture lead ion from water [91]. Different micro plastics adsorption characteristic was examined polyvinyl chloride, polypropylene, polyethylene, polyamides and polyformaldehyde. The previous micro plastics find to be active towered lead, copper and cadmium ions adsorption [92]. Heavy metals removed by using modified cellulose from Pineapple Leaf Fiber. Cellulose extracted from pineapple and treated with EDTA and carboxymethyl to produce Cell- EDTA and Cell- CM that used as adsorbent for lead and cadmium. This was an example of use biomass agricultural wastes as adsorbent [93]. Coal combustion wastes as Coal bottom ash used as adsorbent for heavy metals [94]. Clay and modified clay used as heavy metal adsorbents [95].

The objectives of the study

The general objective of this work is to synthesize cellulose polyurethane foam with ionic functional groups and use it to extract toxic metal ions present in wastewater and other contaminated water.

The sub-objectives include:

1. Convert cellulose to CDA
2. Functionalize CDA with aminobenzoic
3. Develop a method for polymerizing functionalized cellulose with 1,6-hexamethylene diisocyanate and 1,4 phenylene diisocyanate.
4. Characterize the cellulose-based polyurethane by various techniques.
5. Evaluate the efficiency of the cellulose-based polyurethane as an adsorbent for metal ions present in wastewater.

Chapter Two

Experimental

2.1 Instrumentation

The instruments that were used in this study include: a pH meter (JENWAY, 3510), shaking water bath (Daihan Labtech, 20.0 to 250.0 rpm Digital Speed Control), FT-IR Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), Flame Atomic Absorption Spectrometer (Model Zic E-3000 SERIES serial number c11350021 designed in UK AA spectrometer), TGA (Q50 V20.10 Build 36 instrument at a heating rate of 10 °C.min⁻¹ and in N₂ gaseous atmosphere) and Inductively Coupled Plasma Mass Spectrometer ICP-MS (ICE 3xxx C113500021 v1.30).

2.2 Chemicals and reagents

All chemicals were of analytical grade and utilized as received without any further purification. The chemicals are cellulose powder, sodium periodate, methanol, ethanol (99%), p-aminobenzoic acid, sodium borohydride, 1,6-hexamethylene diisocyanate, THF, diisopropylamine, N,N-dimethylacetamide, 1,4-phenylene diisocyanate. All chemicals were purchased from Sigma-Aldrich Chemical Company.

2.3 Synthesis of cellulose-based PUF polymers

2.3.1 Synthesis of cellulose with amine functionality

Two batches of cellulose-based foam were prepared via polyols addition reaction which is an exothermic reaction and required an amine catalyst and additive. The preparation process started with the oxidation of cellulose. Cellulose was converted to dialdehyde cellulose by oxidizing 10.0 g of cellulose using 20.0 g of sodium periodate oxidant in 500 ml of distilled water the reaction container was covered with an aluminum foil to prevent photo-induced decomposition of periodate. The reaction mixture was placed in a water bath at 40 °C and stirred by a mechanical mixer for 24 h. The resulting dialdehyde cellulose was collected and filtrated by using vacuum filtration then it was left to dry in the air.

The next step represents the derivatization of CDA, 1.0 g of CDA was added to a 100 ml round bottom flask followed by the addition of P- aminobenzoic acid and 50 ml of

methanol then the reaction mixture was left in a water bath at 60 °C for 24 h. The resultant Schiff base with imine group was collected by simple filtration then it was moved to vacuum filtration and washed by MeOH. The previous step was repeated with doubling the reactant amounts after 24 h reduction of Schiff base done using 1.0 g of sodium borohydride added stepwise to the reaction mixture, 10 ml of MeOH have added the reaction left with stirring for 4 h then iced water was added to the reaction mixture and filtered via suction filtration the filtrate washed 3 times using EtOH. At the end of these sequence steps, cellulose functionalized with aromatic amine was produced. The final product was collected and dried. The coming step represents the foaming step; two different polymers were prepared via reacting the final product with aliphatic and aromatic diisocyanate compounds.

2.3.2 Synthesis of cellulose-based PUF with aliphatic substitution

Cellulose functionalized with aromatic amine product was reacted with 1,6 hexamethylene diisocyanate to form a 3D structure as a nice foam. Polyurethane foam was prepared by reacting 0.6 g of the cellulose aromatic amine with an excess amount of 1,6 hexamethylene diisocyanate. 0.5 ml of THF was added for good mixing followed by adding 3 drops of diisopropylamine base with stirring for 1 h and a half then 2 ml. After 17 min 0.2 ml of water was added. A few minutes later the foaming process happened, nanocrystalline cellulose-based hexamethylene polyurethane foam (NCC-HMPUF) was washed with DW two times and filtered by vacuum filtration then dried in the air then grinded by blender to a fine powder.

2.3.3 Synthesis of cellulose-based PUF with aromatic substitution

Cellulose functionalized with aromatic amine product was reacted with 1,4 phenylene diisocyanate to form cellulose-based polyurethane foam with aromatic substitution. 0.5 g of 1,4 phenylene diisocyanate was dissolved in DMAc solvent and stirred for an hour then 0.5 g of functionalized cellulose was added. 2 drops of diisopropylamine base, 0.5 ml THF, a 1.5 g of 1,4 phenylene diisocyanate in DMAc was added followed with a 0.2 ml H₂O, after 4 h of continues stirring foam was produced. The final product of nanocrystalline cellulose-based 1,4 phenylene polyurethane foam (NCC- PPUF) was collected, washed two times, filtrated by suction filtration, and dried then grinded by

blender to a fine powder. In foaming experiments amines usually used as catalyst to increase foaming rate.

2.4 Preparation of Standard Solutions

The aim of this step is to prepare several standard solutions to use in batch experiments. A stock solution of lead (II) with a concentration equal to 1000 ppm was prepared by dissolving 0.15985 g of $\text{Pb}(\text{NO}_3)_2$ (MM 331.21 g/mol) in a 100.0 mL volumetric flask. The stock solution was used to prepare several standard solutions of lead (Pb^{+2}) based on dilution calculations $M_1 \cdot V_1 = M_2 \cdot V_2$. The standard concentrations were (1.0, 5.0, 10.0, 15.0, 20.0 and 50.0 ppm). The prepared standards were used to study the effect of various factors on adsorption process effectiveness such as temperature, contact time, polymer dosage, pH, and initial concentration of the contaminate.

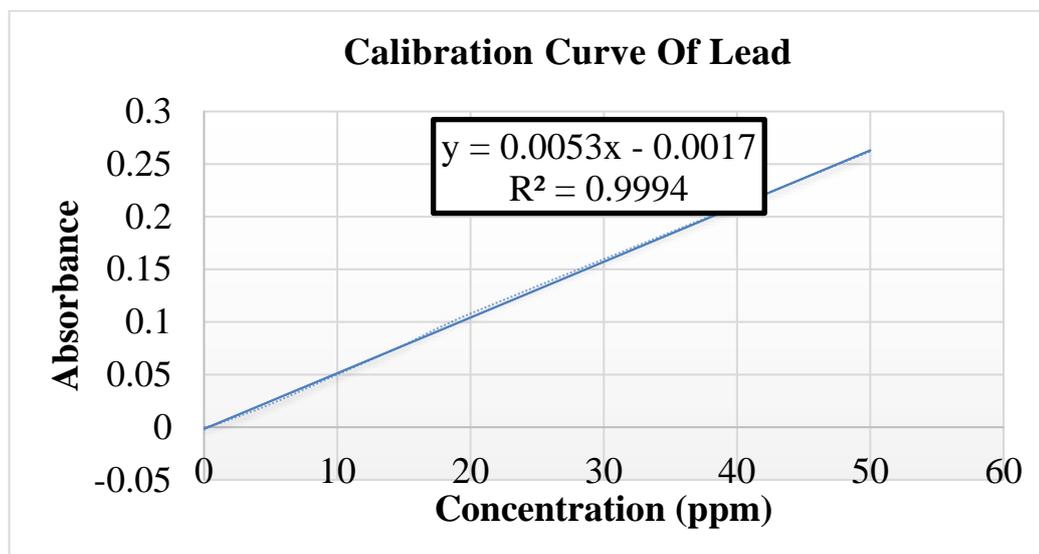
Atomic absorption spectrometer (AAS) instrument was used to conduct the study and determine lead concentration depending upon the resulting calibration curve and instrument measurements.

2.5 Calibration Curve of lead (II)

The calibration curve of Pb^{+2} was created by using the AAS instrument through measuring the different absorbance values for the prepared standard solutions. According to Beer-Lambert law solution with a higher concentration will absorb more light. This law with a calibration curve can be used to determine unknown concentrations based on the directly proportional relationship between absorbance and concentration.

Figure 2.1

Calibration curve of lead Pb^{2+}



2.6 Batch Adsorption Experiments

Batch experiments conducted to evaluate the adsorption on the adsorbent surface. Many adsorption experiments were conducted to test the efficiency of the polymer in heavy metal removal and determine the optimum conditions for adsorption process. Certain amount of the polymer was added to the prepared standards then the solutions with polymer were shaken by using a shaker to make sure that we have a good contact with adsorbent. The previous steps repeated with changing conditions to study the effect of different factor on adsorption process efficiency. Amount of prepared adsorbent (dosage), time, temperature, pH value and metal ion initial concentration were studied to determine the optimum conditions for adsorption. After shaking we predicate that equilibrium was done and adsorption process was accomplished. The coming step was determining the concentration; mixture was filtrated then the solution was ready for testing. AAS instrument was used to detect the concentration of the residue lead ions Pb^{+2} in the filtrate mixture. Adsorption percentage can be calculated according to the instrument measurements using the calibration curve and the equation1 shown below.

$$Y = 0.0053x - 0.0017$$

2.6.1 Effect of contact time

To study the effect of contact time between the adsorbent and the contaminated solution these steps were followed: 250 mg of each polymer was added to six vials contain 10 ml of the 20 & 15 ppm standard solution for NCC-HMPUF & NCC- PPUF respectively, and the mixtures was shaken for different time intervals (1 to 30 min). The samples were then filtered. The concentrations of the metal ion in each sample was determined by AAS.

Table 2.1

Effect of the shaking time for NCC-HMPUF & NCC- PPUF for the adsorption of lead (II) ions.

Adsorbent	Time (min)	Final concentration of Pb (II) (ppm)	Removal (%)
NCC-HMPUF	1.0	13.7	31.3
	5.0	13.2	34.2
	10.0	9.7	51.5
	20.0	7.8	61.03
	25.0	6.331	68.345
	30.0	7.21	63.95
NCC- PPUF	1.0	4.3	71.0
	5.0	4.4	70.6
	10.0	2.5	83.4
	15.0	2.3	84.5
	20.0	3.1	79.0
	25.0	2.1	85.7
	30.0	1.5	90.4

2.6.2 Effect of pH

To study the effect of pH value on adsorption process different adsorption experiment were conducted under pH values ranging from 1 to 12. For each polymer five vials containing 10 ml of 20 ppm standard solution were prepared at certain pH values. pH values were adjusted by using 0.1M of NaOH and HCl solutions. Solutions pH should follow that order two of the vials with basic pH value and two acidic and the last one at pH = 7. After adjusting pH values 250 mg of each polymer were added to each five vials. After shaking for 30 min each sample was filtered off and the concentration of the metal ion was measured by AAS.

Table 2.2

Effect of the pH value for NCC-HMPUF & NCC- PPUF for the adsorption of lead (II) ions.

Adsorbent	pH	Final concentration of Pb (II) (ppm)	Removal (%)
NCC-HMPUF	3.07	11.8	21.1
	4.1	5.4	64.2
	7.7	1.0	93.3
	9.04	0.69	95.4
	11.5	5.7	61.8
NCC- PPUF	2.5	16.3	18.7
	3.08	11.2	43.9
	7.14	0.96	95.2
	11.03	6.8	66.2
	11.8	4.8	75.9

2.6.3 Effect of temperature

Effect of temperature was studied by conducting adsorption experiments under different temperatures. 10 ml of 20 ppm standard solution was added to four vials for each polymer 250 mg of polymer was added to the vials then the mixtures were placed in shaking water bath at the desired temperature (15, 20, 35, 45 °C) for 30 min. At the end of the set adsorption time, the mixtures were filtered, and the concentration of metal ions was determined by AAS.

Table 2.3

Effect of the temperature value for NCC-HMPUF & NCC- PPUF for the adsorption of lead (II) ions.

Adsorbent	Temperature (°C)	Final concentration of Pb(II) (ppm)	Removal (%)
NCC-HMPUF	15.0	5.6	72.1
	20.0	0.32	98.4
	35.0	3.15	84.25
	45.0	5.75	71.23
NCC-PPUF	15.0	0.92	93.9
	20.0	1.14	92.4
	35.0	1.06	92.9
	45.0	1.39	90.7

2.6.4 Effect of adsorbent dosage

In order to find the relationship between the dosage and adsorption efficiency different weights of the prepared polymer was added to vials contain standard with certain concentration. To find the effect of dosage for the first polymer NCC-HMPUF (0.05, 0.1, 0.15, 0.2 and 0.25 g) was added to five vials contain 10 ml of 20 ppm standard solution. The same weights of the second polymer NCC- PPUF was added to five vials containing 10.0 ml of the 15.0 ppm standard solution. The mixtures were placed in a shaker for 30.0 min. After the time was over the concentration of the metal ions was determined by AAS.

Table 2.4

Effect of the adsorbent dosage for NCC-HMPUF & NCC- PPUF for the adsorption of lead (II) ions.

Adsorbent	Wt. of dose (mg)	Final concentration of Pb (II) (ppm)	Removal (%)
NCC-HMPUF	50.00	15.7	21.6
	100.00	14.2	28.8
	150.00	14.7	26.5
	200.00	10.9	45.3
	250.00	8.9	55.3
NCC- PPUF	50.00	2.8	81.5
	100.00	2.5	83.3
	150.00	1.8	87.7
	200.00	1.3	91.25
	250.00	0.98	93.5

2.6.5 Effect of adsorbate concentration

To find the optimum concentration of the adsorbate 10 ml of (5.0, 10.0, 15.0, 20.0, 50.0 ppm) standard solutions were added to five vials, 250 mg of the polymer was added to the vials, then the vials were placed in the shaker for 30 min. these steps were done for the two polymers. Then, the filtrate was determined the ion concentration by AAS.

Table 2.5*Effect of the adsorbate concentrations for the adsorption of lead (II) ions.*

Adsorbent	Initial concentration of Pb (II) (ppm)	Final concentration of Pb (II) (ppm)	Removal (%)	Amount of removal (ppm)
NCC-HMPUF	5.0	1.1	40.5	3.9
	10.0	1.9	43.9	8.1
	15.0	3.0	58.3	12
	20.0	6.31	68.45	13.69
	50.0	27.8	50.0	22.2
NCC-PPUF	5.0	0.59	88.04	4.41
	10.0	0.97	90.3	9.03
	15.0	1.45	90.4	13.55
	20.0	2.29	88.5	17.71
	50.0	23.3	53.39	26.7

2.7 Wastewater purification

In order to test the efficiency and usability of the prepared polymers in real-life sample purification, the two polymers were applied to real samples. The sample was collected from Jericho water; the sample was tested using ICP-MS to detect the present metal ions. After detecting the type and concentration of metal ions the two polymers were applied to the sample to test the efficiency. Two 10 ml of sewage water were added to two vials then the two polymers were applied to it. For each vial, the optimum conditions for the polymer adsorption process were adjusted. A 10 .0 sample from each mixture was collected by a syringe and filtered through a 0.45 μm filter then analyzed by ICP-MS for the residual metal ions.

2.8 Adsorption kinetics

Adsorption kinetics is a very important concept to understand and evaluate the performance of the adsorption process. Determine the model that the data fitted to help in understanding the physicochemical phenomena. The adsorption process is based on the reaction between the adsorbent and sorbet. The reaction is controlled by two types of interaction chemical adsorption which represent the interaction between the electrons and chemical bond formation and physical interaction which is based on attraction between molecules of sorbent and sorbet to describe the kinetic model many models were proposed. pseudo-first-order and pseudo-second-order models are the most widely applied models to study the adsorbent kinetics. Pseudo second-order model can be represented by the linear form via plot t/q_t vs t . The applicability of the model is tested by analyzing data and finding if it follows and is expressed by the Eq.1

$$t/q_t = 1/(K_2 q_e^2) + (t/q_e) \quad \text{Eq.1}$$

where q_t : (mg/g) is the amount adsorbed at time t (min)

q_e : (mg/g) the equilibrium adsorption capacity

k : (g/mg min) the adsorption rate constant.

Pseudo first-order model represented by a linearized form Eq.2

$$\ln(q_e/(q_e - q)) = k_1 t \quad \text{Eq.2}$$

this model will be applied to the data and $\ln((q_e - q)/q_e)$ vs. t is plotted to verify if it obeys the model.

The data should be applied to the two models and the one that gives R^2 value closer to one is valued. If the data is fitted to PFO then the interaction is mostly related to physisorption and if it is fitted to PSO then the chemisorption is the dominant interaction.

2.9 Adsorption Thermodynamic

When we talk about thermodynamics Gibbs free energy, enthalpy and entropy are terms that quickly come to our mind. Thermodynamics determines the spontaneity, and

feasibility and gives an indication of if the reaction is favorable or not. To make a thermodynamic study the following equation is generally used Eq.3

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad \text{Eq. 3}$$

Where ΔG° is the change in Gibbs free energy (J/mol).

ΔH° is the change in enthalpy (J/mol)

ΔS° is the change in entropy (KJ/mol.K).

T equals the absolute temperature (K).

Another eq represents the change in Gibbs energy

$$\Delta G^{\circ} = -R T \text{Ln}K_d$$

$$\text{Where } R \text{ is the gas constant } 8.314 \text{ J.mol}^{-1}\text{K}^{-1} \quad \text{Eq.4}$$

K_d is the thermodynamic equilibrium constant (q_e / C_e) in mol or (L/g).[95]

By combining the previous equations, we can derive the following eq

$$\text{ln}K_d = \Delta S^{\circ}/R - \Delta H^{\circ}/R \quad \text{Eq. 5}$$

Chapter Three

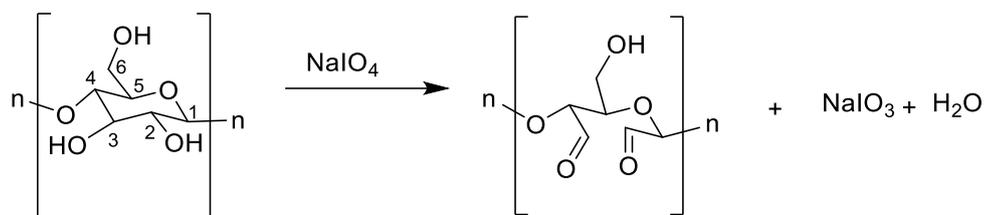
Results and Discussion

3.1 Oxidation of NCC cellulose to 2,3-Dialdehyde Cellulose

To enhance the reactivity of cellulose it is usually functionalized by adding a reactive functional group to the cellulose skeleton. In this work cellulose was converted to more reactive intermediate, cellulose dialdehyde. Cellulose dialdehyde was formed via specific cleavage of the C2-C3 bond. CDA was prepared by periodate oxidation as shown in scheme 3.1

Scheme 3.1

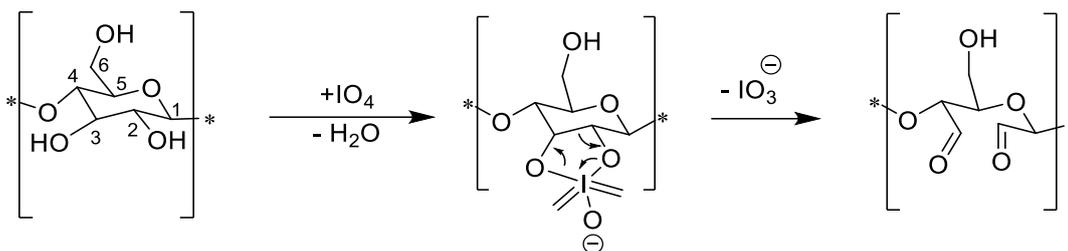
DAC formation by periodate oxidation



As shown in the figure selective cleavage of diol at 2, and 3 positions yielding the 2,3-dialdehyde cellulose groups. One mole of NaIO_4 reacts with one mole of cellulose to produce two aldehyde groups. An excess amount of periodate was used to make sure that the required oxidation level was accomplished. The reaction was carried out in an aqueous dark medium. The formed CDA stayed suspended, and the reaction mixture was considered a heterogeneous solution due to the insolubility of cellulose in an aqueous medium. CDA in an aqueous medium forms a hemiacetal. The reaction mechanism is described in scheme 3.2, 2,3 diol coordinate with periodate anion to form a cyclic intermediate this intermediate rapidly collapsed and CDA is produced by the loss of iodate

Scheme 3.2

mechanism of periodate oxidation of cellulose



3.1.1 Determination of the aldehyde content by titration method

Oxime reaction was used to determine the aldehyde content, a reaction based on a hydroxylamine hydrochloride reaction with an aldehyde group. An aqueous solution of hydroxylamine hydrochloride (NH₂OH.HCl, 5.0% by mass) was prepared by dissolving 1.0 g of hydroxylamine hydrochloride in 20.0 mL of distilled water. The oxidized cellulose was taken to complete the determination process 1.0 g sample of the oxidized cellulose was added to a 50.0 mL of 2-propanol. The mixture was stirred for 10.0 minutes; 10.0 mL of distilled water was then added. A dilute solution of HCl was used to adjust the pH value at 3.5. The mixture was then stirred for another 30.0 minutes. The prepared hydroxylamine hydrochloride solution was added to the cellulose suspension then the mixture was stirred for 6 hr. In the coming step NaOH was used to determine the aldehyde content according to the titration principle, NaOH was titrated with the released hydrochloric acid. 0.5 N of NaOH solution to a pH 3.5 endpoint was used in the titration process. To determine the degree of oxidation and the aldehyde content the following equation was used:

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

Where; [Ald]: the aldehyde content (mmol/anhydroglucose repeat unit).

V_{NaOH}: the volume of NaOH (mL) used in the titration.

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

W_{OC}: the dry weight of oxidized cellulose (g) used in titration.

According to the equation and under the previous reaction conditions calculation showed that the proportion of aldehyde in oxidized cellulose (W_{OC}) was approximately 1.83/anhydrous glucose replication unit.

3.1.2 FTIR characterization of cellulose and CDA

To characterize the aldehyde functional group FTIR was used. From the literature, we can determine the peaks that indicate the presence of aldehyde as shown in the below Figure (Fig 3.1) Appendix A, the Figure show the FT-IR of the oxidized cellulose.

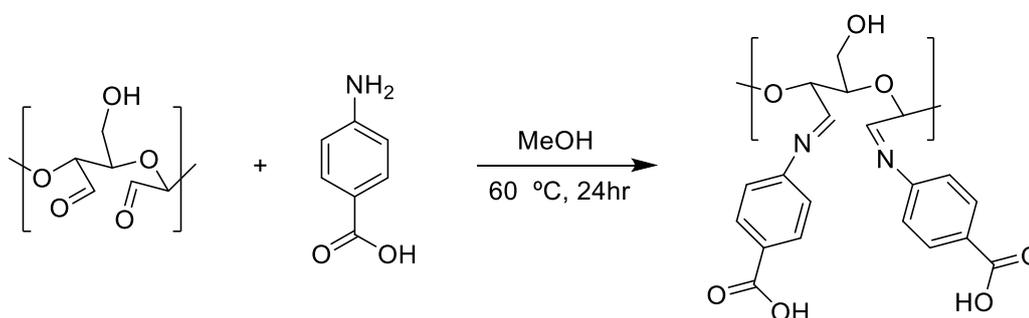
The characteristic bands that can be used as evidence of aldehyde formation band at 1732 cm^{-1} for C=O stretching of aldehyde groups, carbonyl group (H-C=O) stretching band at $1740\text{-}1720\text{ cm}^{-1}$. The detected Absorption peaks were at 3300 cm^{-1} for the vibration frequency of O-H stretching, at 2900 cm^{-1} for CH₂ stretching, at $1600, 1100\text{ cm}^{-1}$ for OH bending vibrations, and C-O stretching respectively. and peaks at 1376 and 1021 cm^{-1} for CH₂ bending and C-O-C stretching vibrations [96,97]. from the FTIR results, hemiacetal presence was detected by finding peaks at 1088 cm^{-1} and forming a broad aldehyde peak.

3.2 Amination reaction of 2,3-dialdehyde cellulose through Schiff's base reaction

The tendency of cellulose to modify increases after converting the hydroxyl group to aldehyde. In this work, CDA was reacted with the aromatic amine (p-aminobenzoic acid) as shown in Scheme 3.3

Scheme 3.3

Preparation of cellulose diaminobenzoic acid

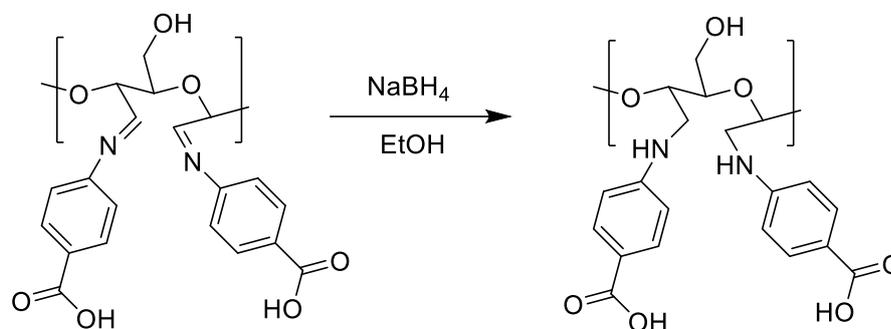


Two moles of amino group compound react per unit of anhydroglucose that contain two free aldehyde groups. The O in aldehyde is replaced by N. The reaction represents nucleophilic addition- condensation reaction it starts with nucleophilic addition of an

amine to the carbonyl. Next, proton transfer proceeds and causes the formation of the O-H bond. Acid protonation of the OH that formed in the previous step converts it to a good leaving group. Water is eliminated and an iminium ion is formed. To get the final imine product nitrogen is gets deprotonated. This reaction is sensitive to H^+ concentration high pH value means that not enough proton to protonate OH and at low pH high concentration of H^+ causes protonation of nitrogen and forms non-nucleophilic species, $R-N^+H_3$. Sodium borohydride was used to complete the amination process. Reductive amination was completed via converting imine Schiff base to an amine by $NaBH_4$ for further reactions.

Scheme 3.4

reduction of Schiff base by BH_4



3.2.1 FTIR characterization of CDA amino acid

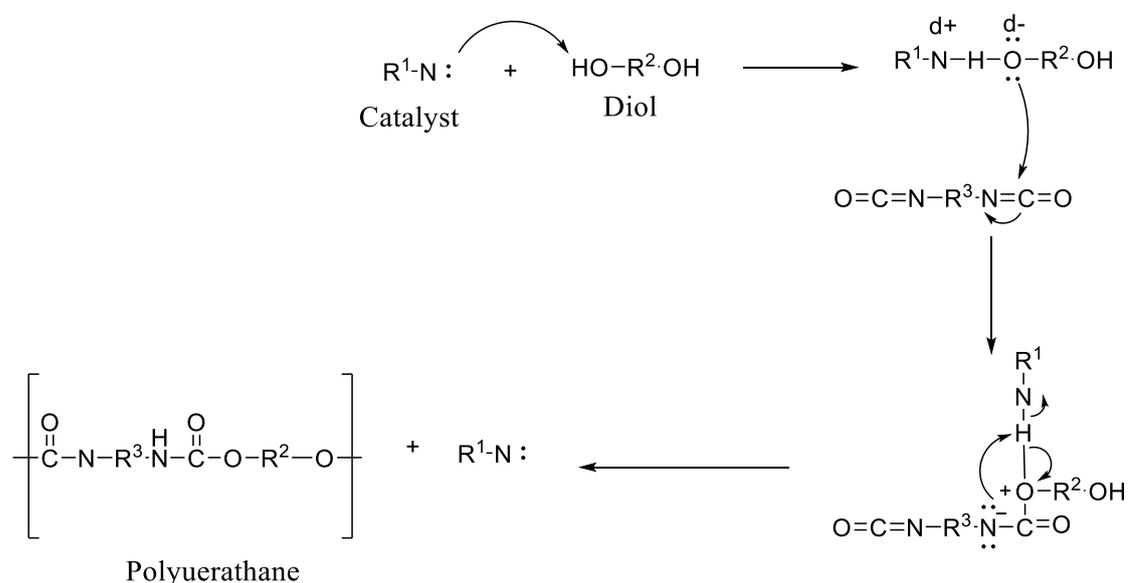
In the amination reaction, the aldehyde group was reacted with the amino group in p-aminobenzoic acid. The Aldehyde group disappeared and converted to the azomethine group. The change in the functional group can be detected by FTIR disappearing of (H-C=O) stretching band at $1740-1720\text{ cm}^{-1}$ and indicate azomethine ($-C=N-$) group stretching absorption band at $1690-1640\text{ cm}^{-1}$ can be used as evidence of imine covalent bond presence and formation of Schiff base. A broad stretching band at 3366 cm^{-1} was detected for OH in the carboxylic acid group. Also, the absorbance band for (C-H) of the aromatic ring was detected stretching vibration at 2906.2 cm^{-1} . In addition, many bands were detected at $1027, 1057, 1529, 1320, 1160,$ and 1606 cm^{-1} for (C-O-C) stretching band of cellulose, C-N group, C=C of the aromatic ring, (C-O of COO^-) bending vibration and (C=O of the COOH) group respectively [98] Figure 3.2 Appendix A.

3.3 Synthesis of cellulose-based PUF polymers

Two polymers were prepared one of them with aliphatic substitution and the other aromatic. The foaming process starts with reacting cellulose amine derivatives with the diisocyanate by adding diisopropyl amine as a catalyst. The electron pairs on amine attack H on alcohol and form H – bond. O now has a partial negative charge so it can attack the electron-poor carbon on isocyanate this step results in positively charged oxygen and negative charge nitrogen. Urethane is formed by swiping the hydrogen using nitrogen. The Scheme below (Scheme 3.5) shows a detailed mechanism of the reaction.

Scheme 3.5

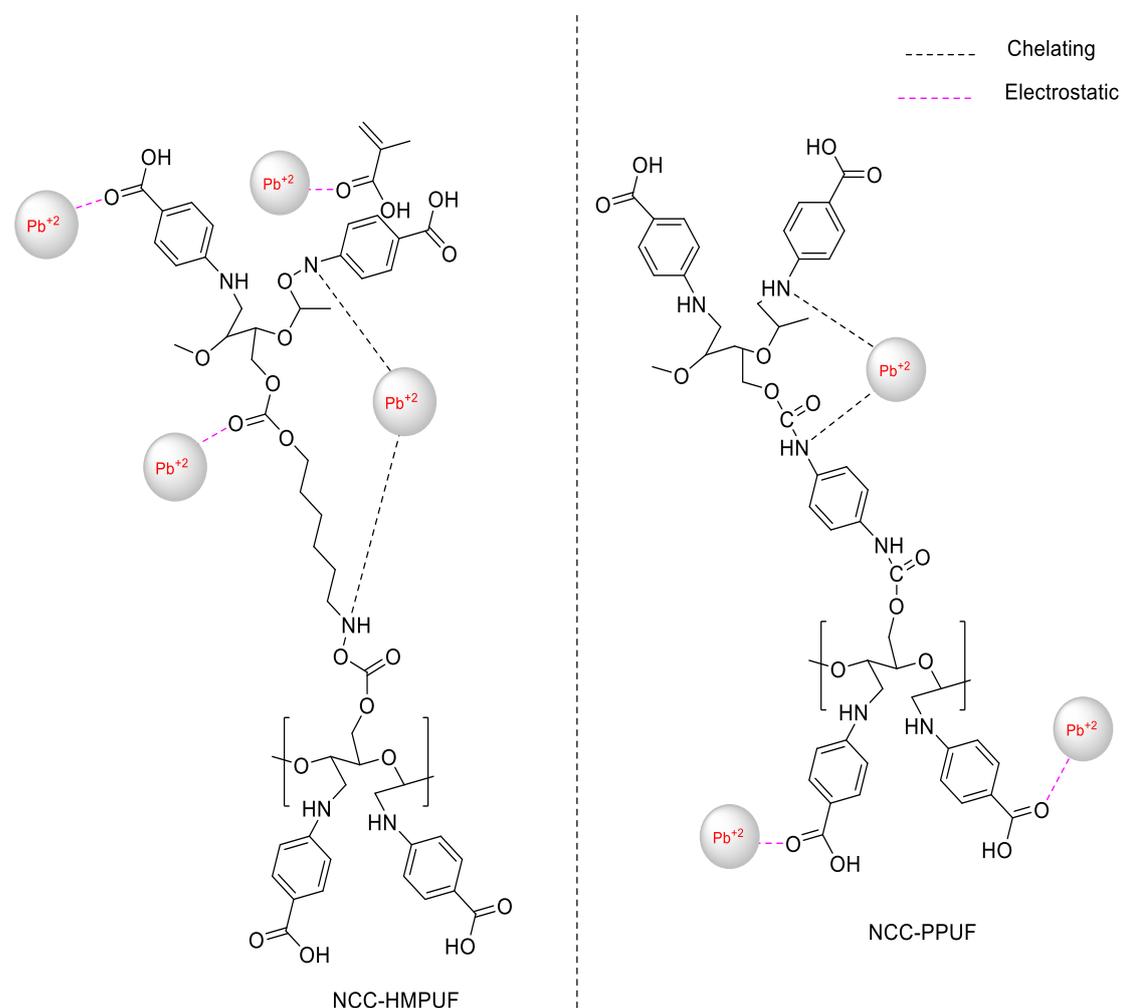
General illustration of polyurethane formation reaction steps



Scheme 3.6 shows the two polymers with the produced active sites. Two factors affect the adsorption process chelating and electrostatic force. N in the urethane linkage is a chelating active site. C=O functional groups with high electron density on oxygen atom acts as an electrostatic active site. The two polymers were prepared via reacting the final product in the previous section with 1,4 phenylene and 1,6 hexamethylene diisocyanate to produce cellulose-based foam with aromatic and aliphatic functionalities respectively, the polymers were named as NCC-HMPUF & NCC- PPUF, respectively.

Scheme 3.6

cellulose-based foam polymers with binding sites



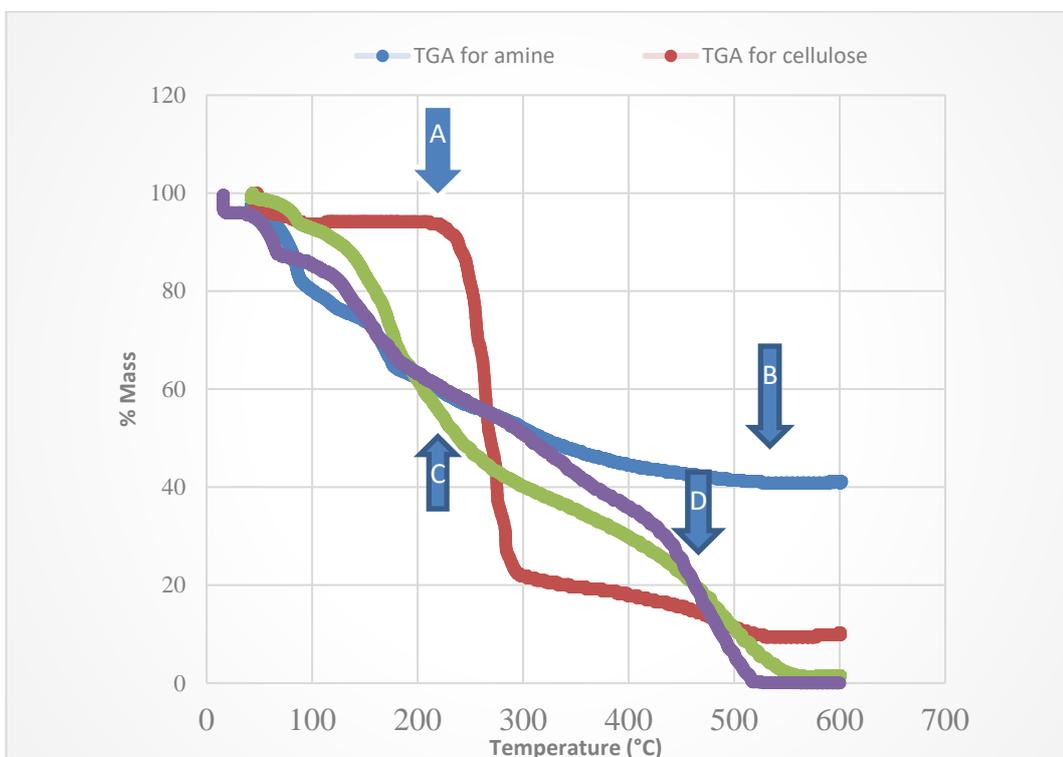
Many peaks can be used as evidence of PU foam formation peaks of urethane linkage at 3300 cm^{-1} for N-H, at $1650, 1550\text{ cm}^{-1}$ for CO-NH and NH_2 . For C-O peak at 1100 cm^{-1} . Figure 3.3 Appendix A shows FT-IR for the first polymer with aromatic functionality *NCC-PPUF*. In addition, the functional groups of the second polymer *NCC-HMPUF* with the aliphatic substitution were detected by FTIR as shown in figure 3.4 Appendix A. The peak at 3333.12 cm^{-1} is for N-H bond which is an indication of a condensation reaction between OH and CNO, C=C aromatic ring at 1508.72 cm^{-1} , also C-H stretching vibration band 2933.63 cm^{-1} was observed from the methylene group, vibration band of C-O alkoxy observed at 1261.8 cm^{-1}

3.4 Thermal Gravimetric Analysis (TGA)

Thermal analysis is very important to make a judgment on the stability of the prepared polymers under different temperatures. TGA was used to analyze each product in the sequence of reaction steps. As shown in Figure 3.5 For cellulose and cellulose dialdehyde, CDA will show high decomposition rates due to the lower crystallinity as a result of glucopyranose ring opening. The well crystalline structure of cellulose prevents it from melting. Cellulose starts losing weight after 250 °C while CDA is decomposed after 100 °C. Imine (Schiff base) starts to decompose below 100 °C and shifts to a lower temperature that's main the thermal stability decreases. Amine is the most thermally stable product from the graph we could realize that the decomposition rates shifts to higher temperatures. The amine starts to decompose slightly below 100 °C and the decomposition rate becomes constant for a while that is repeated until 450°C was reached the decomposition stopped and the %mass was around 40%.

Figure 3.5

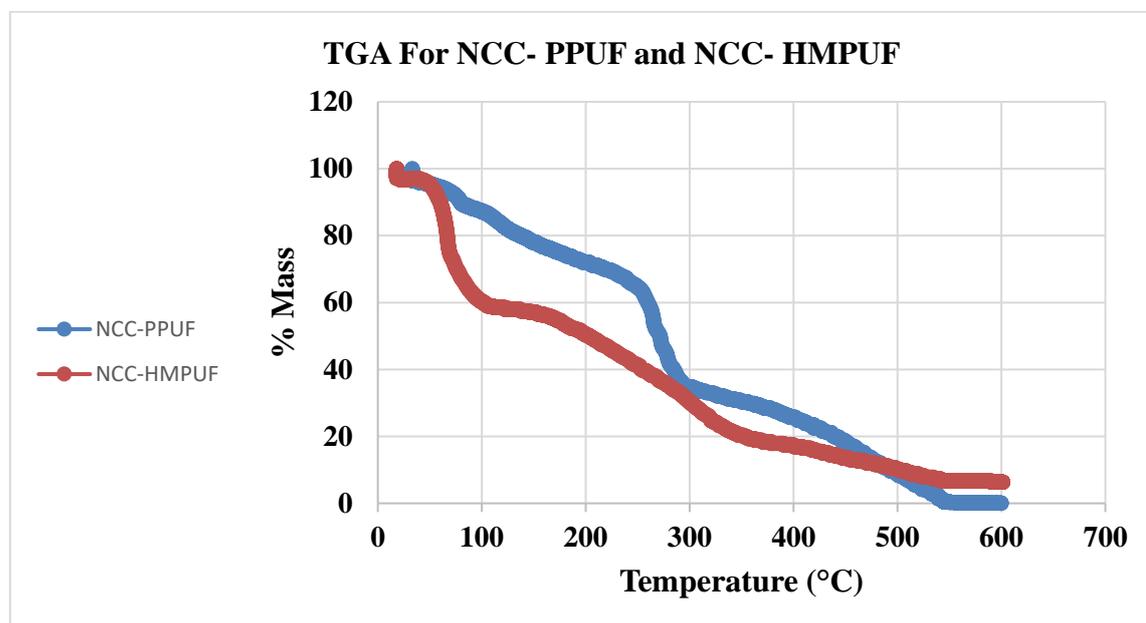
TGA analysis for the reaction intermediate products A for cellulose, B for amine, C for CDA, and D for imine.



In addition, TGA was used to analyze the thermal stability of the two polymers as shown in Figure 3.6. Losing the weight below 100°C is related to the removal of volatile content such as water. For the first polymer NCC-HMPUF losing the weight initiated below 100°C. losing weight rate was slowly and become constant at certain temperature then it re-decrease again. At 400°C the rate of decomposition becomes narrow and the % of the mass was approximately 10. The second polymer shows higher thermal stability between 40-500 °C then its stability decrease and vanishes. The thermal stability of PUF products is based on the urethane linkage and the rigidity of the structure. The type of diisocyanate used for preparation also affected the thermal stability. The chain flexibility in HMPUF is higher than in PPUF due to the presence of the methylene group which has less rigidity than caused by the aromatic ring in PPUF. The flexible structure shifts decomposition rates to a lower temperature. By comparing the TGA for cellulose and cellulose-based foam we can realize that foaming increases the thermal stability of cellulose due to the formation of homogeneous networks.

Figure 3.6

TGA for PPUF and NCC- HMPUF polymers



3.5 Adsorption results

Two polymers were prepared, and their adsorption efficiency was studied and compared via adsorption experiments. In addition, the optimum adsorption process conditions were determined for each polymer. The major tool for all experiments was the AAS instrument that was used for the determination of residue heavy metal concentrations. Adsorption percentage was calculated based on the initial and final concentration and followed the equation: adsorption % = $\frac{C_i - C_f}{C_i} \times 100\%$

Where C_i : the initial concentration of the heavy metal ion (ppm).

C_f : the final concentration of the heavy metal ion (ppm).

The adsorption capacity was also calculated according to the following equation $q_e = \left(\frac{C_i - C_f}{m}\right) * V$

Where; V : the volume of solution (L).

m : the mass of adsorbent (g).

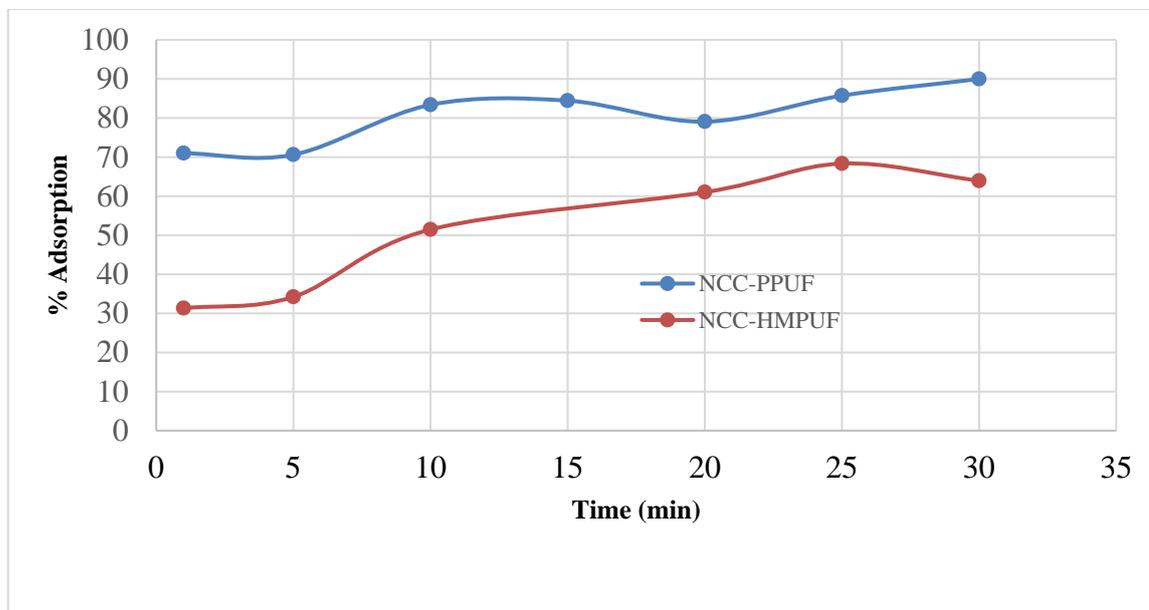
the adsorption capacity for the two polymers was compared by using different concentrations of the heavy metal ions.

3.5.1 Effect of contact time

To detect the optimum contact time between the lead ion and each adsorbent of the two polymers, % of removal was measured as a function of time as shown in (Figure 3.7). The figure shows an increase in the adsorption rate over time.

Fig 3.7

Effect of contact time on the adsorption of Pb^{+2} ion on NCC-PPUF & NCC-HMPUF ($C_i = 20$ & 15 ppm for NCC-PPUF & NCC-HMPUF respectively, adsorbent dose = 0.25 g, volume of soln. = 10.0 mL, at room temperature).



This plot shows that the highest % of adsorption for NCC-PPUF adsorbent reached 90.35 % after 30 minutes of shaking, then the optimum contact time for that polymer is 30 min. The % of adsorption was increased over time. while for the other adsorbent NCC-HMPUF, the plot shows that the optimum contact time was 25 min at which the maximum % of adsorption was achieved 68.345 %. The decrease in adsorption rate after a certain time is due to the occupation of all the binding sites. At first, the contaminants molecules fill the outer surface (the nearer binding sites) then they tend to fill the inner pores which make the adsorption slowly and need more time.

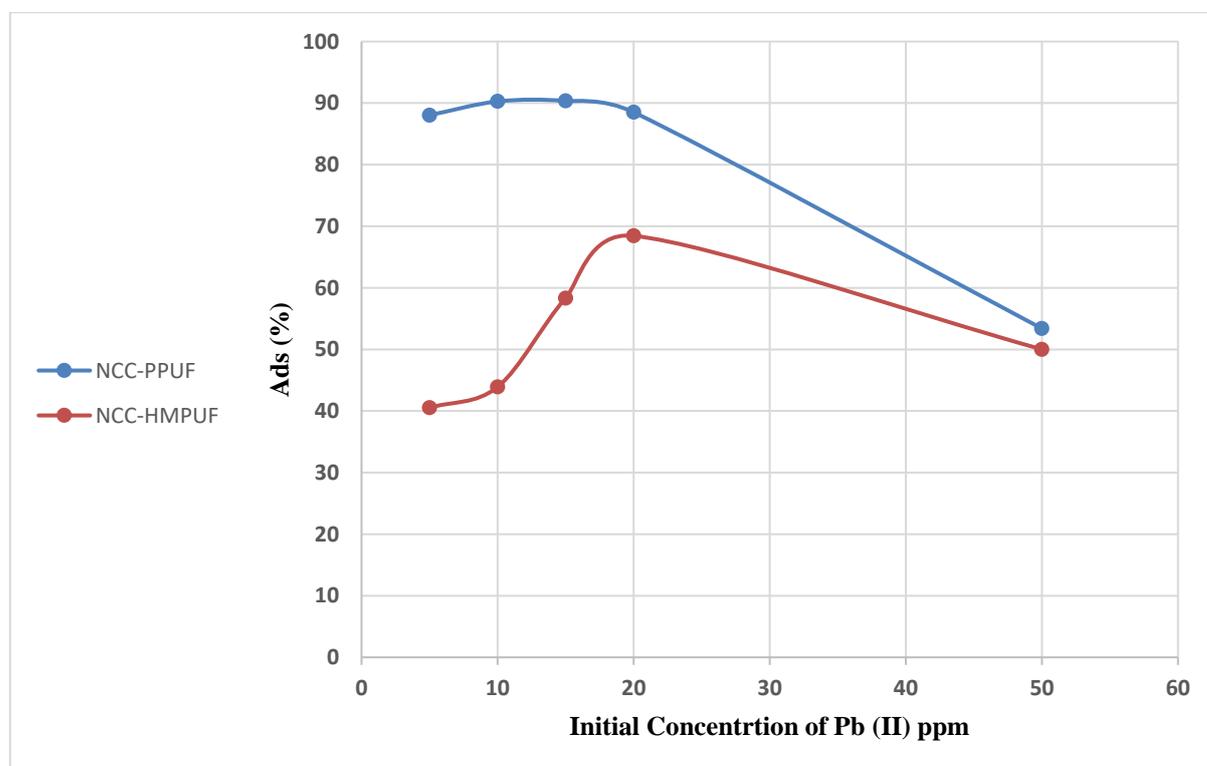
3.5.2 Lead initial concentration effect

Different samples of standard solutions with different concentrations (5.0, 10.0, 15.0, 20.0, 50.0 ppm) were prepared. The polymers were applied to the samples at fixed conditions of pH, temperature, dosage, and contact time. To study the relationship between initial Pb^{+2} concentration and % of adsorption a plot of % removal vs initial Pb^{+2} concentration was figured out. For the first polymer *NCC-PPUF* Figure 3.8 shows that the % of adsorption increased by increasing initial lead concentration the highest percent of removal 90.35 % was at 15.0 ppm of lead then the % removal decreased. The second

polymer *NCC-HMPUF* was influenced by concentration increasing clearly. The maximum % of removal 68.4% was at 20.0 ppm. The Figure shows increase in adsorption by lead concentration increase until certain limit then it decreased. General explanation for adsorption process tracking the higher lead initial concentration provide adsorption process with a driving force to push more particle to the polymer surface. At higher lead concentration more Pb^{+2} will be adsorbed and diffused to adsorbent surface. The previous case remains true until reach a certain concentration at which all the binding sites saturated.

Figure 3.8

Effect of Lead concentration on the adsorption of Pb^{+2} by HMPUF & PPUF- NCC



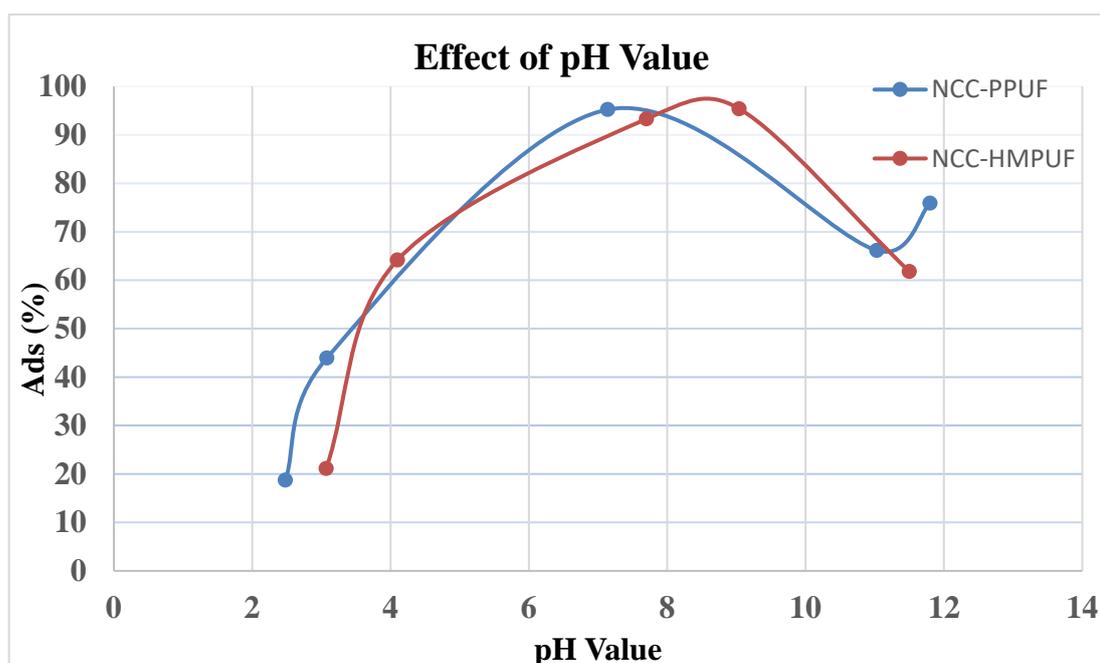
3.5.3 Effect of pH

pH is a very important factor that affects the adsorption process performance. pH value affects the adsorbent surface, ionization of the materials in the solution, and the functional groups in the binding sites. For the two polymers at low pH value, acidic medium the polymer shows low adsorption % these could be due to damage to the polymer, the high H^+ concentration that competes with the metal ion and occupied the binding sites, and cause protonation of the functional groups that work as binding sites. In addition, an

acidic medium such as HCl is reported in the literature as an eluent used to remove heavy metals [99]. At pH 7 the two polymers show high adsorption rates it's a neutral medium where N-H has the best conditions for chelating and works as a binding site. The first polymer PPUF has the highest adsorption percentage 95.255% at pH 7 and the second polymer HMPUF has a high % of adsorption 93.29%. A higher pH value causes an increase in the negative charge density on the functional groups at binding sites which increases adsorption rates. In addition, at a high pH value, the functional groups such as carboxyl are deprotonated. The second polymer shows the highest % of adsorption 95.38% at pH 9. The excessive increase of pH value decreases the adsorption rates due to hydroxyl complexes formation that reduces the adsorption efficiency. Figure 3.9 shows the relationship between pH value and % of adsorption.

Figure 3.9

Effect of pH value on the adsorption of Pb^{+2} by PPUF/HMPUF



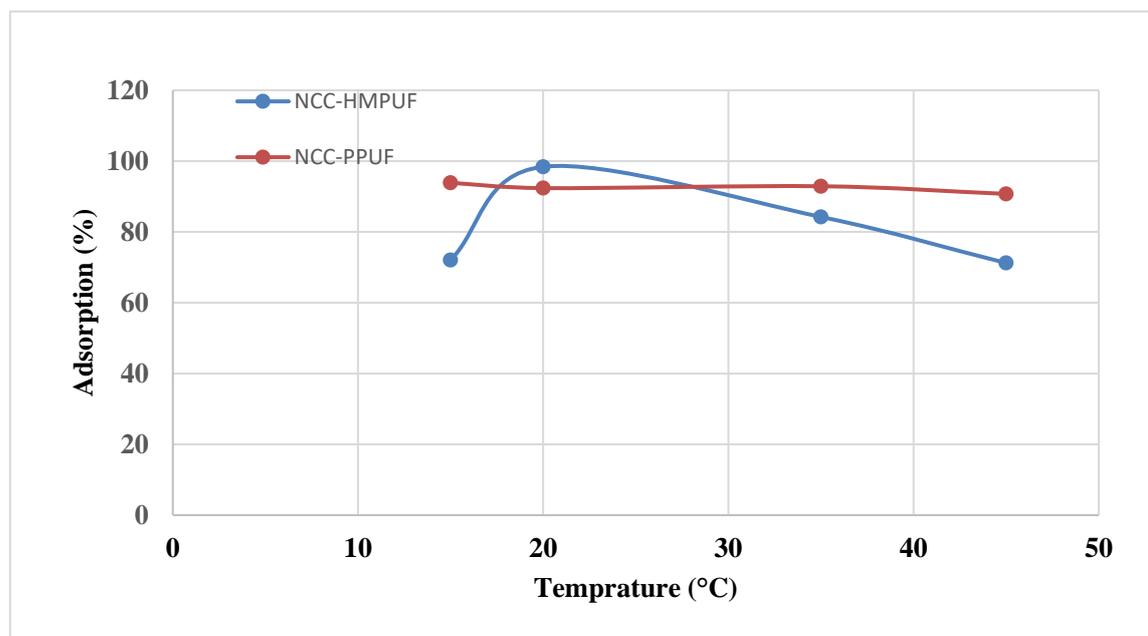
3.5.4 Temperature Effect

The general trend of the relationship between adsorption rate and temperature is that the adsorption rate will decrease at a high temperature. The first polymer shows a lower response to the temperature increase this may be related to the adsorption process type. According to the results, we predicted that the adsorption process at the NCC-PPUF surface is controlled by the chemical interaction between the lead and adsorbent surface

(chemisorption). Chemisorption can take a place at high temperatures and it's irreversible. The highest adsorption percentage of 93.88% was at 15 °C and it is slightly affected by increasing the temperature the percentage at 45 °C was 90.74%. NCC-HMPUF polymer is highly affected by increasing the temperature it seems that it follows physical adsorption which reversible process. The increase in % of adsorption from 72.05 to 98.42 % when the temperature goes from 15 to 20 °C can be interpreted because of porosity increase and increased pore volume. Then at 35 & 45 °C, the adsorption percentage was dropped to 71 % which related to the reversibility of the adsorption process. The molecules can't be fixed at a certain position at the adsorbent surface. At high temperatures, the molecules get kinetic energy, and so on it's free to move. Figure 3.10 shows the relation between T and adsorption percentage.

Figure 3.10

Effect of Temperature on the adsorption of Pb^{+2} by PPUF/HMPUF

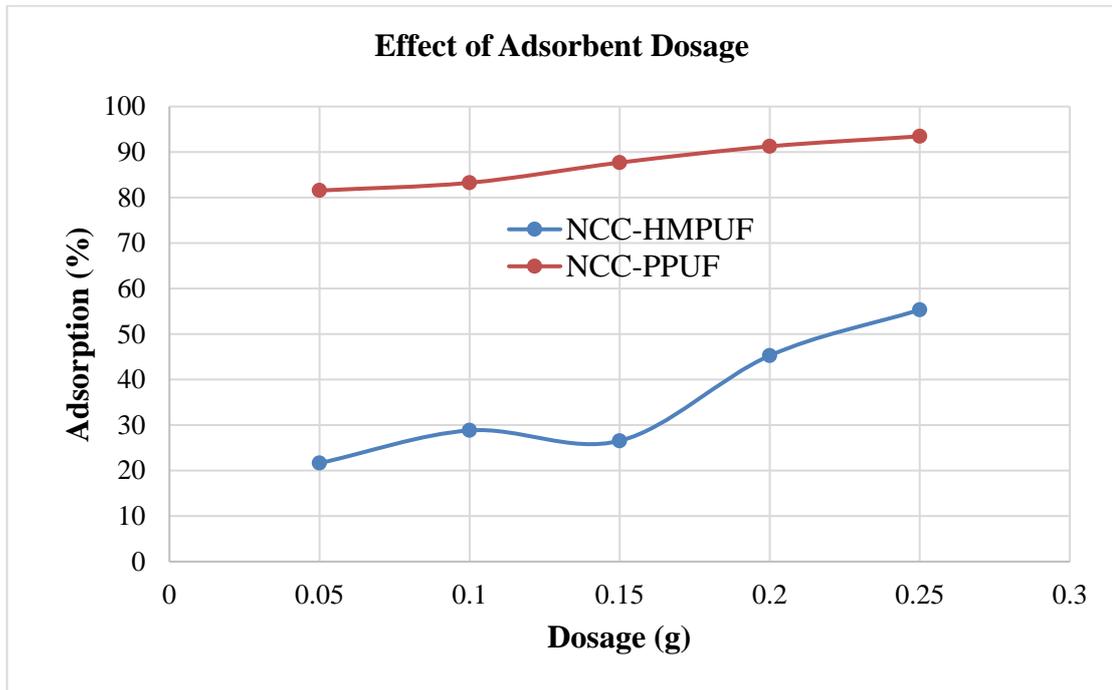


3.5.5 Adsorbent Dosage Effect

The relation between dosage and adsorption % for the two polymers was studied and the Adsorption % vs dosage was figured out. For NCC-PPUF the highest adsorption 93.5% was at 0.25 g, and for HMPUF it was 55.3235% at 0.25g. The results show an increase in the heavy metal removal with increasing the dosage of the adsorbent because of increasing the number of active sites for the removal. Figure 3.11 shows the relation between dosage and adsorption percentage.

Figure 3.11

Effect of Adsorbent Dosage on the adsorption of Pb²⁺ by PPUF/HMPUF



3.6 Optimum adsorption parameters

Optimum adsorption parameters are shown in table 3.1

Table 3.1

Optimum Adsorption Parameters

Optimum condition/ Adsorbent	Initial lead concentration (ppm)	Parameters pH, Temp (°C), Contact time (min), and Adsorbent dosage (mg)
PPUF	15	7, 15, 30, and 0.25
% of removal = 90.5%		
HMPUF	20	9, 20, 25, and 0.25
% of removal = 95.4 %		

3.7 Adsorption isotherm

Many models were proposed to understand the equilibrium isotherm. One parameter isotherm and two parameters isotherm are usually used to interpret the isotherm. Langmuir and Freundlich were applied to the derived data from the experiments to

investigate the performance of the polymers in the adsorption process. The models are mainly designed to study and determine the amount of sorbet adsorbed per unit of mass to the adsorbent surface at a particular temperature.

3.7.1 Langmuir adsorption isotherm

The linear form of the eq is the following

$$C_e/q_e = 1/q_m k_e + C_e/q_m \quad \text{Eq.5}$$

C_e where; is the concentration of adsorbate at equilibrium (mg g^{-1}).

K_L is Langmuir constant related to adsorption capacity (mg g^{-1}). [100]

K_L is an expression of the adsorption capacity it is affected by the surface area and porosity of the adsorption. As the surface area and pore volume increase, the capacity will increase.

K_L is used to calculate a dimensionless constant called R_L separation factor it can be calculated from eq.6

$$R_L = 1/1 + K_L + C_0 \quad \text{Eq.6}$$

Where K_L is Langmuir constant (mg g^{-1}) and C_0 is the initial concentration of adsorbate (mg g^{-1}). [101]

R_L value gives an indication of the reaction if it is favorable or not if it equals 1 then it is linear, favorable, $1 > R_L > 0$ favorable, unfavorable $R_L > 1$ and irreversible if $R_L = 0$

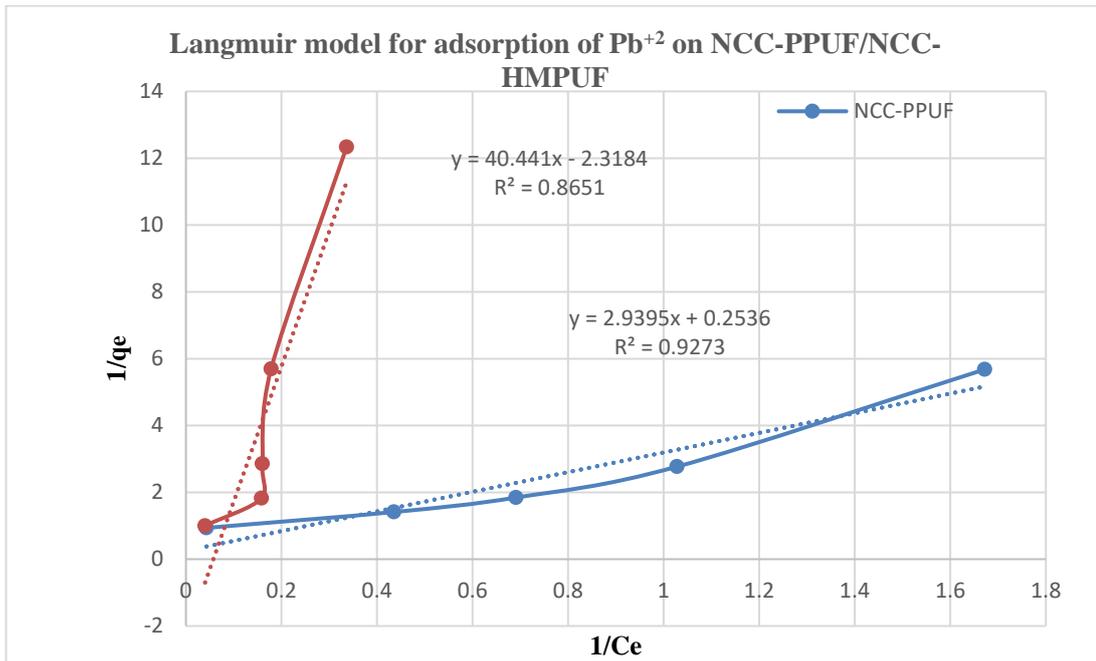
$1/q_e$ Vs $1/C_e$ plotted to apply the adsorption parameters to Langmuir adsorption isotherm.

After representing data and deriving the equation of the linear line the following equation 7 compared with the line equation

$$1/q_e = 1/Q_{\max} + 1/b Q_{\max} (1/C_e) \quad \text{Eq.7}$$

Figure 3.12

Langmuir model for adsorption of Pb²⁺ on PPUF/HMPUF



the R value is less than 1 for PPUF so the adsorption process is favorable, for HMPUF R is greater than 1 so the adsorption is unfavorable. Figure 3.12 represent Langmuir model plot and the isotherm parameters are shown in table 3.2 Appendix B

3.7.2 Freundlich adsorption isotherm

Freundlich adsorption isotherm deals with the distribution of active sites and their energies. And it is applicable for the adsorption process on the heterogeneous surface. The linear form of the model equation as:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad \text{Eq. 9}$$

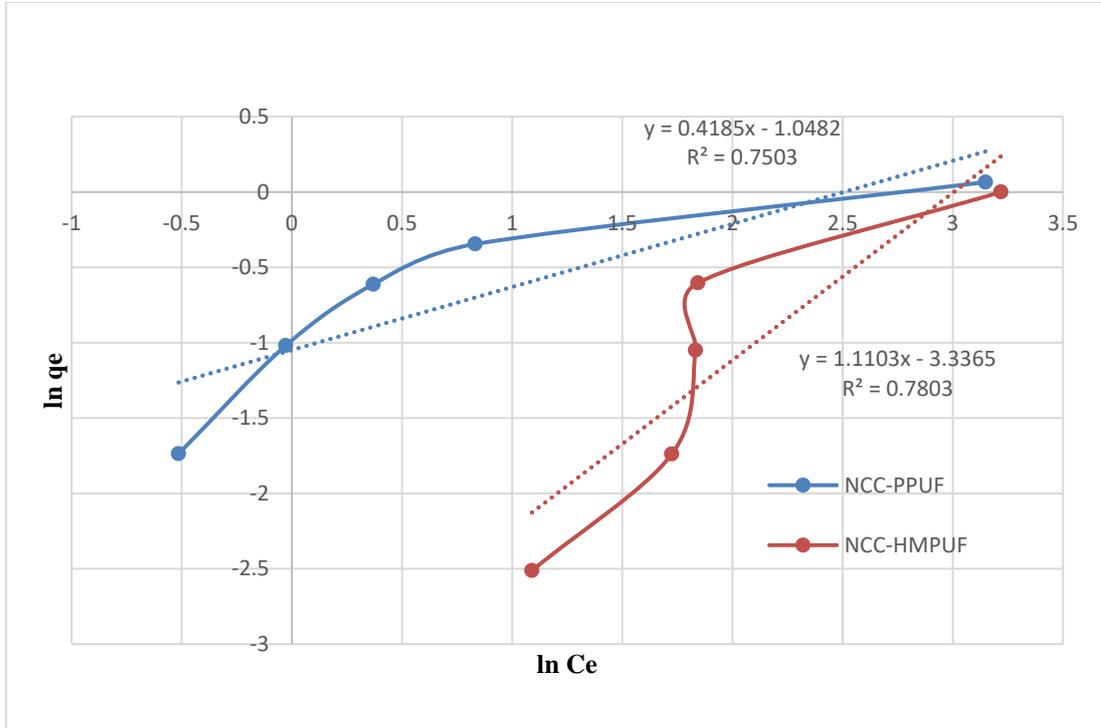
where q_e is the amount of the adsorbate (in mg) that is adsorbed per unit mass (g) of adsorbent; Q_{\max} is the maximum adsorption capacity, and n and k_f are constants that depend upon the nature of the adsorbate and adsorbent, where n represents the adsorption intensity and k_f represents the adsorption capacity (mg g^{-1}). [102]

By comparing the R^2 value after applying data to the isotherm models for the two polymers the values were found nearer to 1 in Langmuir isotherm model so it can be realized that the data are fitted to this model, and it regulates the adsorption of Lead (II)

ions on the surfaces of polymers. Freundlich model plotted in Figure 3.13 and the adsorption isotherm parameters are shown in table 3.3 Appendix B.

Fig. 3.13

Freundlich model for adsorption of Pb^{+2} on PPUF/HMPUF



3.8 Adsorption Kinetics

The data were applied to two adsorption kinetics models Pseudo first order PFO and pseudo-second order PSO to test which one of the two models the data will be fitted to.

3.8.1 pseudo-first order model

The following equation is the linear form that will be compared to the linear line equation after plotting $\ln (q_e - q_t)$ vs t

$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad \text{Eq .10}$$

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

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

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

Pseudo first order model is represented in Figure 3.14 Appendix A and the kinetic parameters are listed in table 3.4.

Table 3.4

Adsorption kinetic parameters (pseudo-first order model) for the adsorption of Pb (II) on PPUF/HMPUF.

Adsorbent	Adsorption kinetic pseudo-first order model			
	R ²	Theo. q _e	Exp. q _e	K ₁
NCC-PPUF	0.6644	1.002	0.5421	0.106
NCC-HMPUF	0.458	1.9	0.54735	0.1557

3.8.2 pseudo-second order model

This model relates the uptake of the contaminant to the available surface sites. The linearized form of the PSO equation as:

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad \text{Eq. 11}$$

K₂: the second-order rate constant (g mg⁻¹ min⁻¹)

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

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

To test the model validity t/q_t plotted vs t [103]

Pseudo second order model is represented in Figure 3.15 Appendix A and the kinetic parameters are shown in table 3.5.

Table 3.5

Adsorption kinetic parameters (pseudo-second order model) for the adsorption of Pb (II) on PPUF/HMPUF.

Adsorbent	Adsorption kinetic pseudo-second order model			
	R ²	Theo. q _e	Exp. q _e	K ₂
NCC-PPUF	0.9925	0.5369	0.5421	1.92
NCC-HMPUF	0.9799	0.583	0.547356	0.4926

The R^2 value for the two polymers are very close to 1 in PSO model so it can be concluded that the data are fitted to Pseudo-second order model.

3.9 Adsorption Thermodynamics

As shown in the table 3.6 and from the calculated values of thermodynamics parameters NCC-HMPUF adsorbent is an endothermic process ($\Delta H > 0$) and spontaneous ($\Delta S > 0$). And for NCC-PPUF adsorbent it is an endothermic process ($\Delta H > 0$) and spontaneous ($\Delta S > 0$) the negative value of ΔS indicates that the randomness will not increase during adsorption process in the solid surface [104]. To complete the thermodynamic study Vant's Hoff plot is figured out in Figure 3.16 Appendix A.

Table 3.6

The thermodynamic parameters for the adsorption of Pb (II) on PPUF/HMPUF.

Adsorbent	Temp.(K)	Adsorption Thermodynamics		
		ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol.K)
NCC-PPUF	289.15	-9.11	7.693	31.44
	294.15	-9.27		
	309.15	-9.74		
	319.15	-10.05		
NCC-HMPUF	289.15	-31.03	28.725	107.2
	294.15	-31.56		
	309.15	-33.17		
	319.15	-34.25		

3.10 Adsorption study on a Real-life sample

The two polymers were applied to water samples from Jericho sewage water at optimum conditions of the adsorption. The concentration of many heavy metals was detected after and before applying the polymer. ICP- MS was used to determine the heavy metals ion concentrations. Table 3.7 shows % of removal of many metals. A high % can be observed for most of the metals ion. For Pb^{+2} NCC-PPUF polymer removes 90.49% of the ions and for HMPUF the % of removal was 95.43%. lead ions recorded high adsorption rates for the two polymers even in real samples with the presence of many ions can compete with it. From the results, we can say the two polymers achieved excellent adsorption performance.

Table 3.7*ICP-MS results from the water research center*

Metal ions	Conc. Of Jerico sample (ppm)	Initial Conc for HMPUF (ppm)	Initial Conc for PPUF (ppm)	% of removal for HMPUF (ppm)	% of removal for PPUF (ppm)
Ag	0.016	0.003	0.002	79.62	90.44
Al	52.691	0.408	0.605	99.22	98.85
Ba	1.396	0.112	0.23	91.94	83.499
Be	0.008	0.003	0.003	64.15	58.44
Bi	0.224	0.014	0.0334	93.95	85.049
Ca	1530.203	270.109	549.842	82.34	64.06
Co	0.029	0.00006	0.001	99.79	95.017
Cr	0.372	0.161	0.09	56.79	75.69
Cu	1.564	0.046	0.035	97.05	97.7
Fe	69.821	1.341	6.485	98.07	90.71
Ga	0.031	0.006	0.009	80.64	71.612
K	211.035	75.247	140.484	64.34	33.43
Li	0.143	0.047	0.079	67.25	44.48
Mg	568.719	121.233	264.595	78.68	53.47
Na	2309.026	1743.408	1614.193	24.49	30.09
Ni	14.202	8.534	11.661	39.906	17.89
Pb	0.159	0.007	0.015	95.43	90.49
Rb	0.284	0.08	0.149	71.77	47.59
Sr	5.401	0.986	2.329	81.73	56.86
Tl	0.003	0.0002	0.00008	92.8	96.8
U	0.025	0.002	0.004	90.08	85.16
V	1.211	0.548	0.879	54.72	27.40
Zn	8.819	0.169	0.155	98.07	98.24

3.11 Conclusion

Cellulose-based foam polymers were successfully prepared starting from cellulose oxidation and conversion to cellulose dialdehyde. Sequence steps were followed to reach the final products with urethane linkage and amino benzoic acid functionalities. The resultant product in each step was analyzed by TGA & FTIR to test the thermal stability and make sure that the aimed functional group was produced. After synthesizing the two polymers a batch extraction experiment was carried out to determine the adsorption conditions that leads the highest removal efficiency 90.5 & 95.4 % for PPUF & HMPUF respectively. For NCC-PPUF the optimum conditions are pH 7.0, temperature 15 °C, time 30.0 min, and dosage 0.25 g. For the second polymer pH 9.0, T 20 °C, time 25.0 min, dosage 0.25g. After detecting the optimum conditions polymers were applied to a real sample and the two polymers show excellent efficiency in the removal of heavy metals. In addition, thermodynamic and kinetic studies were conducted. After studying the adsorption kinetic parameters, the two polymers were fitted to pseudo-second order model. The thermal studies show that the adsorption process of the two polymers is exothermic ($\Delta H^\circ < 0$). From all the results we can conclude that the combination of amino benzoic acid cellulose with urethane linkage produces an outstanding cellulose-based foam adsorbent. Cellulose-based foam adsorbent is an efficient attractive choice that can be used in water treatment from heavy metals ion. The goal of the study was achieved we can be benefited from the aspects of polyurethane foams and modify the cellulose surface to create an efficient adsorbent at a low cost.

List of Abbreviations

Abbreviation	Meaning
CDA	Cellulose dialdehyde
NCC	Nanocrystalline cellulose
AC	Activated carbon
CMCF	carboxymethylated cellulose fiber
CMCNFs	carboxymethylated cellulose nanofibrils
EPA	Environmental Protection Agency
IQ	intelligence quotient
OISW	olive industry solid waste
PUF	Polyurethane foam
PU	Polyurethane
WHO	World Health Organization
LCD	Liquid crystal film
R ²	Correlation coefficient (regression coefficient, fitting coefficient)
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
FAAS	Flame Atomic Adsorption Spectrometer
% Ads.	Percent Adsorption
Soln.	Solution
NCC-HMPUF	Nanocrystalline cellulose-based hexamethylene polyurethane foam
NCC- PPUF	Nanocrystalline cellulose-based phenylene polyurethane
Wt.	Weight
Temp.	The temperature (°C)
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)
K ₁	The pseudo-first order rate constant
K ₂	The pseudo-second order rate constant
K _f	Freundlich constant
K _l	Langmuir isotherm constant (L/mg)
K _d	The thermodynamic gas constant
1/n	Dimensionless Freundlich constant giving an indication of how favorable the adsorption process
R _l	Dimensionless constant separation factor
ΔH°	The change in enthalpy
ΔS°	The change in entropy
ΔG°	The change in Gibbs free energy
R	The universal gas constant
T	The Absolut temperature

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Appendices

Appendix A

Figures

Figure 3.1

FTIR of dialdehyde cellulose

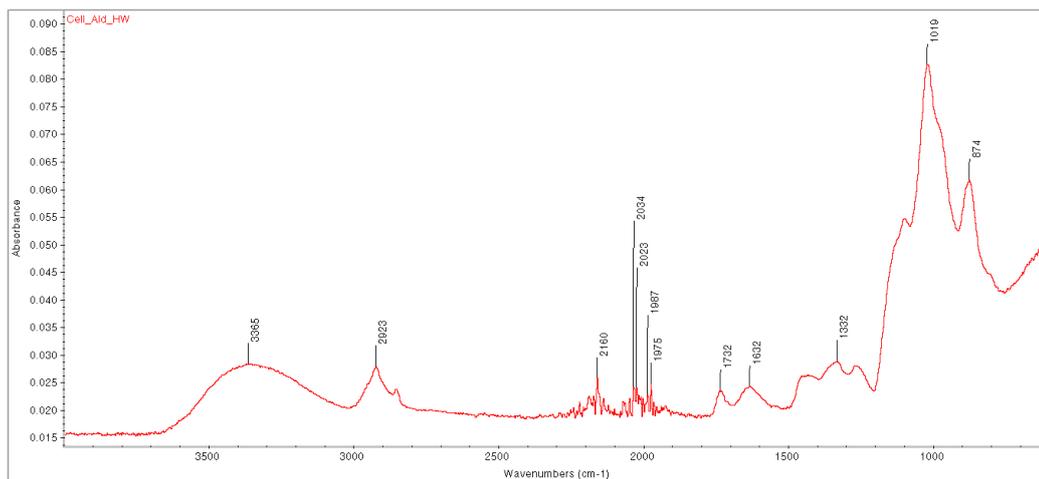


Figure 3.2

IR spectrum for the Schiff base.

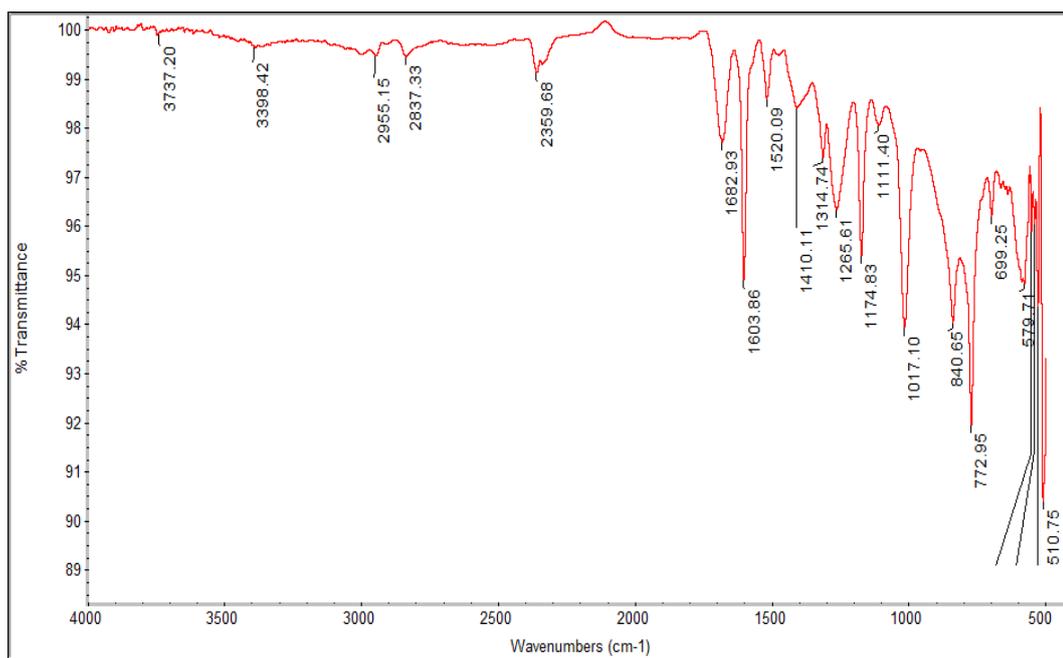


Figure 3.3

IR for the first polymer NCC- PPUF

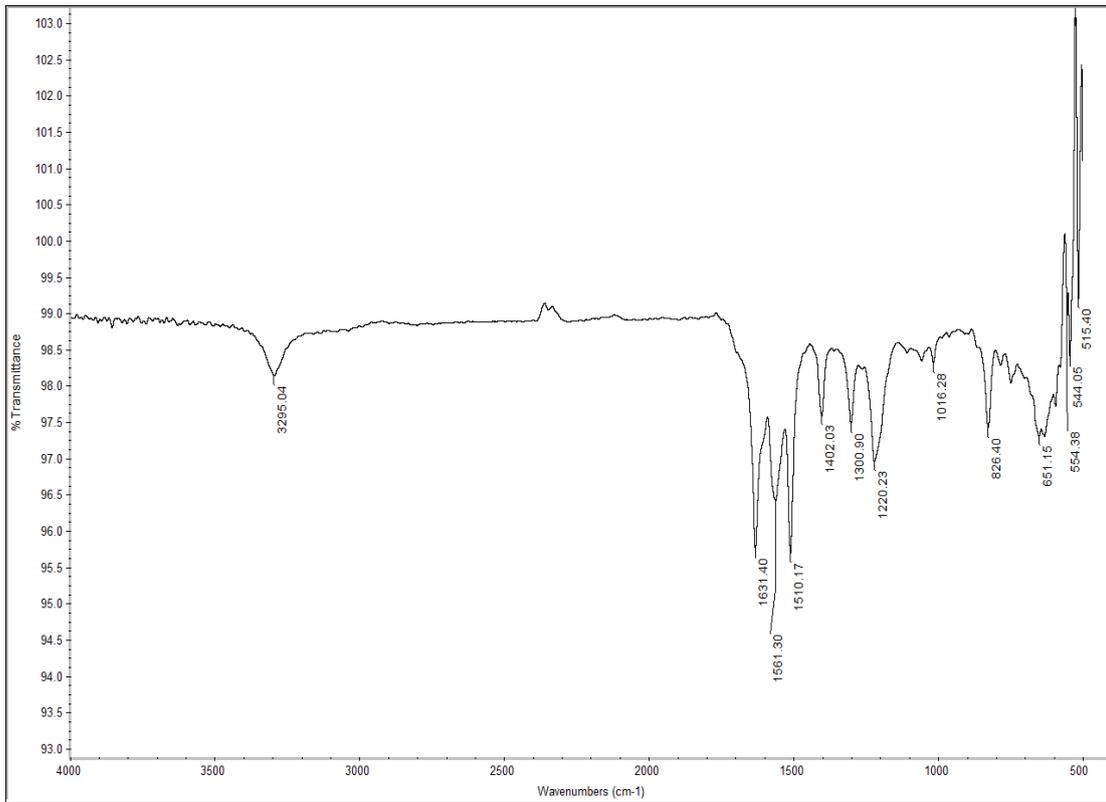


Figure 3.4

IR for the second polymer NCC- HMPUF

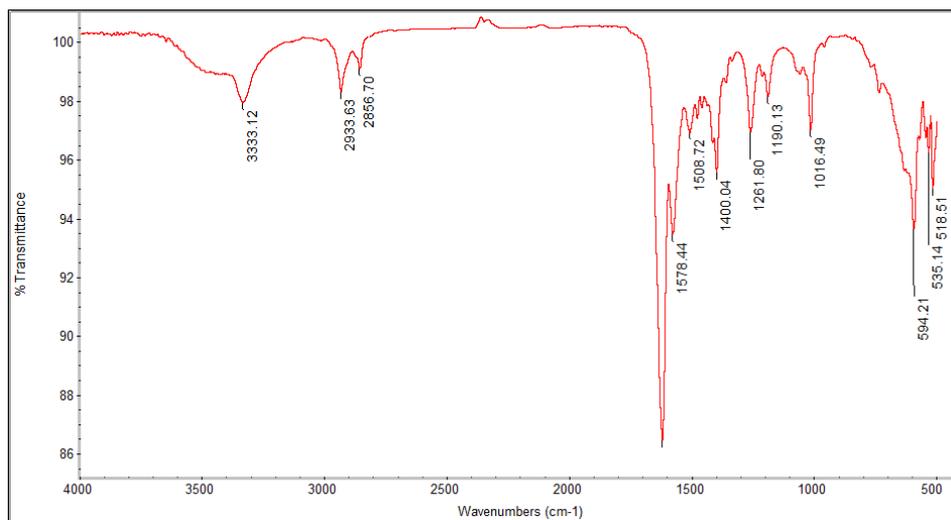


Fig. 3.14

Pseudo-first order model for the adsorption of Pb^{2+} on NCC-PPUF/NCC-HMPUF.

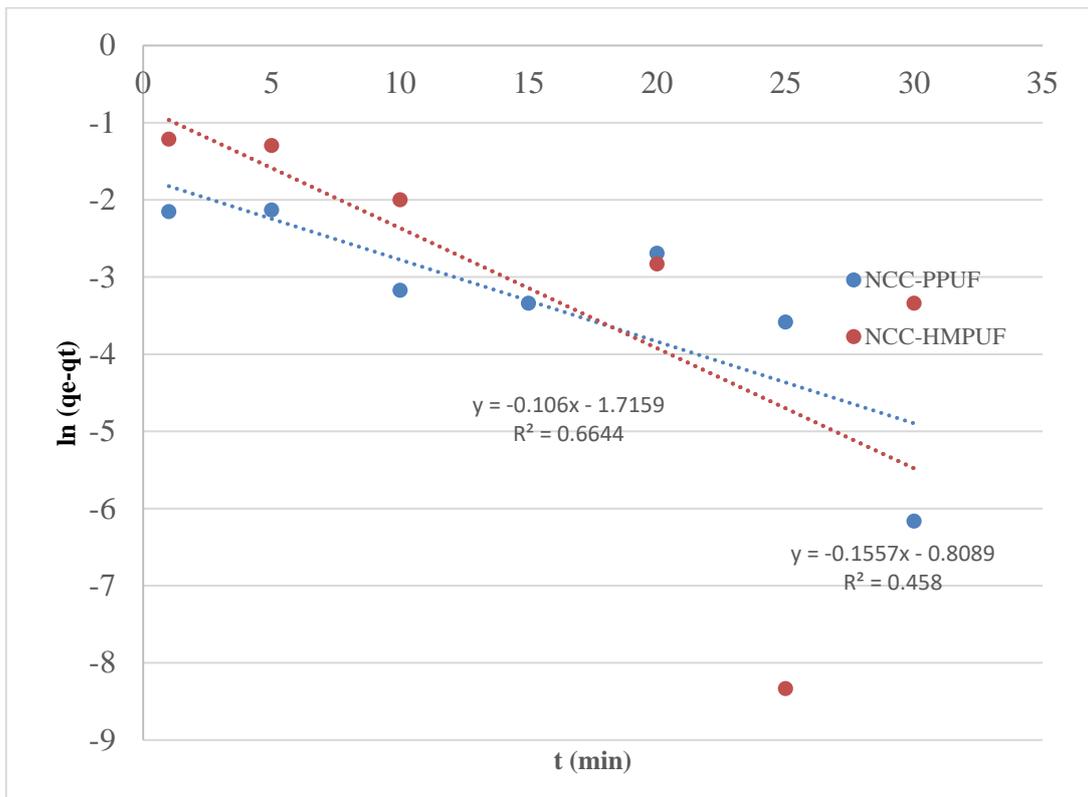


Fig. 3.15

Pseudo-second order model for the adsorption of Pb^{2+} on PPUF/HMPUF

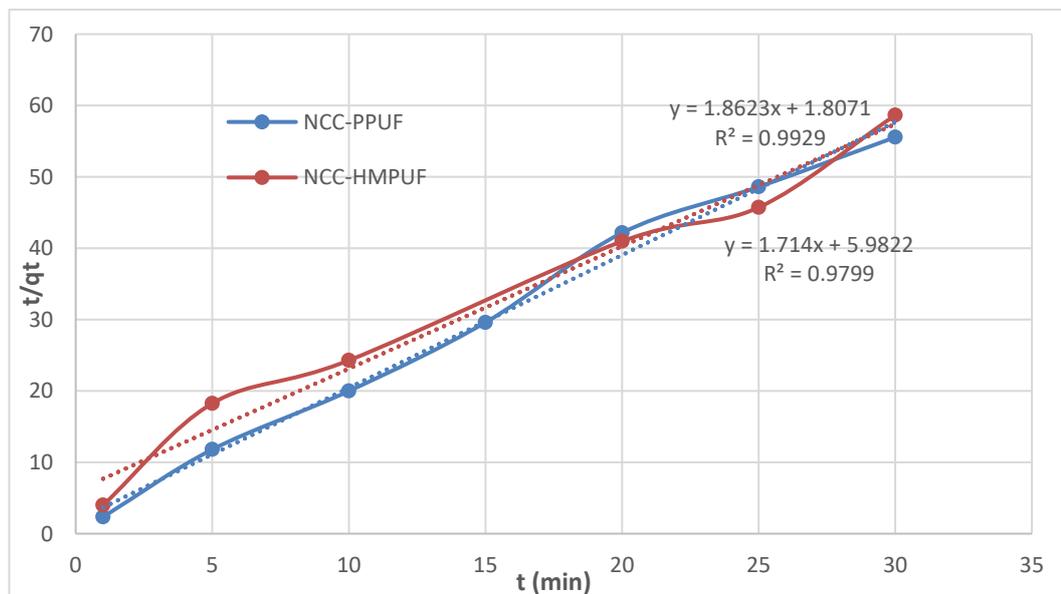
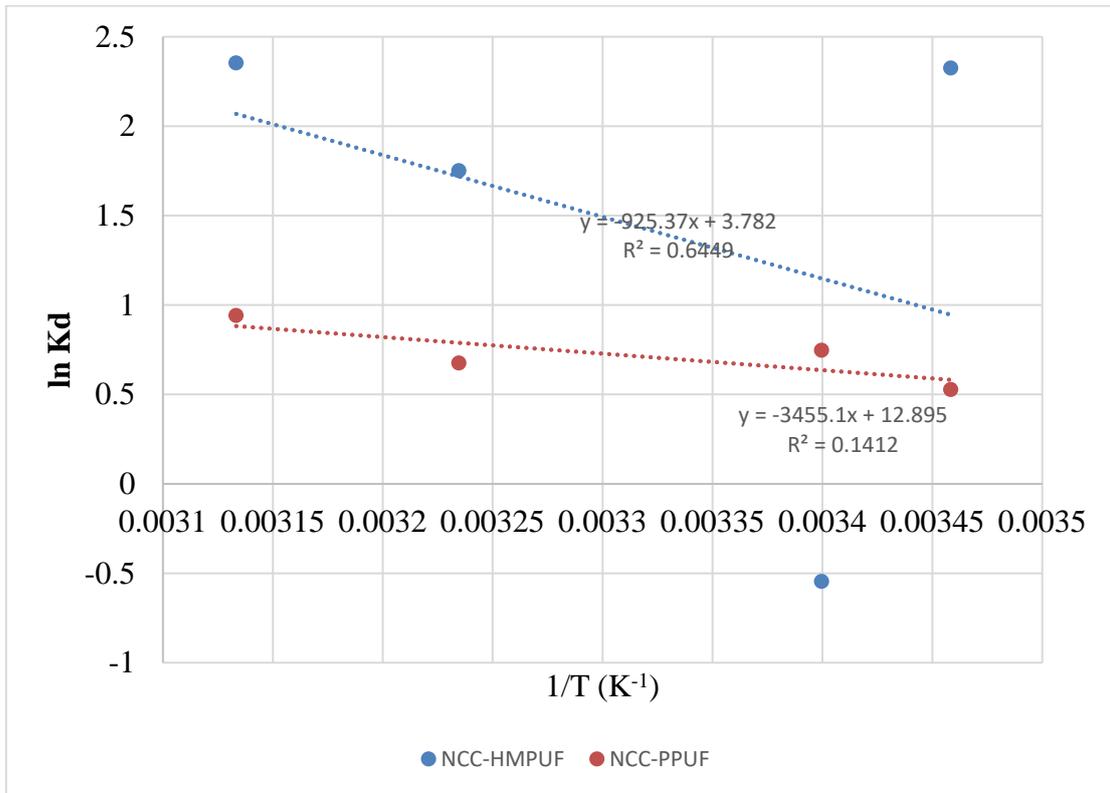


Fig. 3.16

Van't Hoff plot for the adsorption of Pb(II) on PPUF/HMPUF



Appendix B

Tables

Table 3.2

Langmuir Adsorption isotherms parameters for NCC-PPUF/NCC-HMPUF.

Adsorbent	Langmuir R²	Q_{max}	K₁	R₁
NCC-PPUF	0.9273	3.94	0.086	1.775
NCC-HMPUF	0.8651	0.43	0.057	0.122

Table 3.3

Freundlich Adsorption Isotherms parameters for PPUF/HMPUF.

Adsorbent	Freundlich R²	N	K_f
NCC-PPUF	0.7503	2.3894	1.678
NCC-HMPUF	0.7803	0.9006	0.618



جامعة النجاح الوطنية
كلية الدراسات العليا

الرغوة المعتمدة على السليلوز بوجود مجموعة وظيفية أيونية:
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قدمت هذه الرسالة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء، من كلية الدراسات العليا، في
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الملخص

الخلفية: أدى الاستخدام المفرط للمواد الكيميائية واستخدامها في مجال واسع من التطبيقات إلى زيادة نسبة الملوثات في الماء. تشكل الملوثات العضوية والمعادن الثقيلة والملوثات غير العضوية خطراً كبيراً على حياة الكائنات. تعتبر أيونات المعادن الثقيلة من أكثر الملوثات شيوعاً وضرراً. كرس العلماء جهودهم لإيجاد طريقة فعالة واقتصادية ومتاحة تجارياً وصديقة للبيئة لإزالة الملوثات من المياه.

الهدف: في هذه الدراسة، نستفيد من خصائص رغوة البولي يوريثان PUF حيث يعد من المواد سهلة التحضير والاستخدام في تنقية المياه. الهيكل المسامي المرن الذي يمكن التحكم فيه، شكل قابل للتعديل، عملية تحضير بسيطة، ثبات عالي، ومعدل امتصاص عالي. هذه الخصائص تجعله مناسباً جداً للاستخدام كمادة ماصة للأيونات المعدنية السامة. أدى عدم وجود مجموعات وظيفية فعالة لربط المعادن في PUF إلى الحد من استخدامها في تنقية المياه الملوثة.

المنهجية: في هذه الدراسة سيتم تصنيع PUF المعدل بمجموعة وظيفية أيونية مرتبطة به تساهمياً واستخدامه في عملية الامتزاز للمعادن. تم تحضير PUF عن طريق بلورة مركب ثنائي أيزوسيانات مع السليلوز المؤكسد. تضمنت الخطوة الأولى تفاعل السليلوز المستخرج من الجفت مع بيبيونات الصوديوم لإنتاج السليلوز المؤكسد المحتوي على مجموعتي الديهايد. تم مفاعلة السليلوز المؤكسد المنتج مع حمض بارا أمينوبنزويك لتكوين قاعدة شيف. تم اختزال قاعدة شيف بواسطة بوروهيدريد الصوديوم لتكوين سليلوز معدل

يحتوي على مجموعة أمين. في الخطوة الأخيرة، تمت إضافة مركب ثنائي أيزوسيانات لتشكيل رغوة بهيكل ثلاثي الأبعاد ومحتوية على الكربوكسيل. إن وجود مجموعات الكربوكسيل وحمض البنزويك الأميني بالإضافة إلى خصائص PUF الأخرى المذكورة أعلاه يجعل الرغوة المحضرة مادة جديدة بخصائص فريدة ومميزة لتتقية مياه الصرف الصحي. تم تشخيص البوليمرات المحضرة باستخدام TGA و FT-IR. تم استخدام الرغوة الناتجة في استخلاص الأيونات المعدنية من مياه الصرف الصحي. تم إنشاء الطريقة المثلى لتتقية مياه الصرف الصحي باستخدام بوليمرات السليلوز PUF المحضرة. تم تحديد ظروف الامتزاز التي أدت إلى أعلى فعالية من خلال عمل تجارب الاستخلاص بظروف مختلفة مثل: الرقم الهيدروجيني، و وقت التلامس ، ودرجة الحرارة °C ، و كمية المادة ، و تركيز أيون المعدن الأولي.

النتائج: تمت دراسة كل معامل من خلال تغيير قيم المعامل مع الحفاظ على ثبات المعاملات الأخرى. تم تحديد المعاملات التي أدت إلى أعلى فعالية وكانت كالتالي درجة الحموضة 7.0.9.0 ووقت التلامس 30. و 25 دقيقة ودرجة الحرارة 15.20 والجرعة 250 ملغم وتركيز أيون المعدن الأولي 15.0.20.0 جزء في المليون لكل من PPUF و HMPU على التوالي. تم استخدام أداة التحليل الطيفي للامتصاص الذري AAS لتحديد تركيز الرصاص بعد ضبط البوليمر تحت ظروف معينة. بعد الكشف عن المعاملات المثالية، تم تطبيق تجربة البوليمرات المحضرة على عينة حقيقية من مياه الصرف الصحي. في ظل الظروف المثلى، تم اختبار كفاءة البوليمرات في إزالة الرصاص. تم استخدام مطياف كتلة البلازما المقترن بالحث-ICP MS لتحديد تركيز الملوثات في عينة المياه (مياه الصرف الصحي) بعد تطبيق البوليمر وقبله. تم دراسة نموذج Langmuir وتطبيق على بيانات عملية الامتصاص. تم استخدام نموذج Van't Hof لتحديد قيم ΔH° و S° و G° كانت -7.6935 و -31.44 و 9.53 و -28.725 و -107.2 و 32.4 ل PPUF و HMPUF- NCC على التوالي. تشير النتائج إلى أن عملية الامتزاز تتم بشكل تلقائي في درجة حرارة الغرفة. أظهرت الدراسة الحركية أن العملية تتبع نموذج pseudo second order حيث إن قيمة R^2 للبوليمرين قريبة جدًا من 1.

الخلاصة: بعد تحديد الظروف المثلى، تم تطبيق البوليمرات على عينة من الحياة الواقعية واطهر البوليمران

فعالية وكفاءة ممتازة في إزالة المعادن الثقيلة.

الكلمات المفتاحية: المعادن الثقيلة، تلوث المياه، السليلوز، رغوة البولي يوريثان، الامتزاز.