An-Najah National University
Faculty of Graduate Studies

CELLULOSE WITH URETHANE CROSS-LINKS DECORATED WITH IONIC FUNCTIONAL GROUP FOR WASTE WATER PURIFICATION FROM TOXIC METAL IONS

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Dedication

To my Beloved dad and mom, thank you for being my guiding light and source of endless support. Your sacrifices and loves have shaped me into who I am today wishing them both lives long filled with happiness and good health.

To my brother & Sisters my lifelong companions who have supported me through every step of my life Thank you for being the siblings I could always count on.

To my soulmate husband Rabei, greatest supporter thank you for helps and cooperation.

Also, to my second family, my husband's family.

I humbly dedicate this thesis to my innovative teachers who have always provided me with crucial knowledge during my studies.

I am appreciative of everyone who has been and continues to be in my life for their love and support.

Acknowledgment

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Also, I would like to thank all of the professors, the chemistry labs supervisor, and laboratory technicians at An-Najah National University for their cooperation, and helped me earn my master's degree.

Declaration

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

CELLULOSE WITH URETHANE CROSS-LINKS DECORATED WITH IONIC FUNCTIONAL GROUP FOR WASTE WATER PURIFICATION FROM TOXIC METAL IONS

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

Student's Name Shorouq Nezar Ahmad Khaseeb

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Date: 25/04/2024

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Abstract

Background: water is elixir of life. Excessive chemical use in varies sectors, whether in industry, agriculture or other, can result in an increased load of pollutants in water. Radionuclides, household chemicals, pharmaceuticals and personal care products (PPCPs), microorganisms, plumbing inorganic chemicals, and other contaminants are common in water. Heavy metals are among the most harmful of these pollutants owing to their lasting effects, and toxicity even at low concentration. As a result, removing these hazardous heavy metal ions from water is becoming crucial.

Objectives: The purpose of this thesis is to establish novel adsorbent material based on polyurethane foam (PUF) that was enhanced with an ionic functional group capable of efficiently absorbing harmful metals from water.

Methodology: The process of creating the target polymers included a series of chemical reactions between carboxymethyl cellulose (CMC) and diisocyanate compounds (hexamethylene diisocyanate & phenylene diisocyanate) in the presence of diisopropyl amine as a catalyst, resulting in the formation of the foam polymeric materials carboxymethyl cellulose hexamethylene polyurethane foam (CMC-HMPUF) and carboxymethyl cellulose phenylene diisocyanate polyurethane foam (CMC-PPUF) with urethane links.

Results: The adsorption capacity of polymeric foams toward Pb(II) was assessed using a variety of parameters such as temperature, pH, adsorbent dose, time and initial ion concentration.

In addition, the optimal value of each of the parameters that resulted in quantitative elimination of Pb(II) were discovered. The percentage removal of Pb(II) by CMC-HMPUF polymer was around 95%, while CMC-PPUF was approximately 93%.

Adsorption thermodynamics, kinetics, and isotherms were also studied to gain insight into the mechanism and spontaneity of adsorption. The result demonstrate that the adsorption of Pb(II) process is classified exothermic process ($\Delta H^\circ<0$), and spontaneous at low temperatures ($\Delta G^\circ<0$),($\Delta S^\circ<0$).

The obtained isothermal and kinetic values illustrated that the adsorption by the two foams fit the Freundlich model, and obey a Pseudo-second order kinetic.

The created foams exhibited a great propensity to remove multi-metal ions found in an actual sample of sewage water.

Conclusion: The goal polymers were made, and urethane linkages were detected using IR spectroscopy, the two polymers foam showed strong thermal stability, they were effective in removing heavy metals from wastewater.

Keywords: Polyurethane, CMC, heavy metals, hexamethylene diisocyanate, phenylene di isocyanate.

Chapter One

Introduction

1.1 Overall Review

Water is a vital and necessary component of all life on earth, it is essential for the survival of all living species, including humans.

Globally freshwater demand has been growing fast due to how populations and economies have grown. Furthermore, temperature, rainfall, evaporation rates, plant type, soil quality, and water runoff are all key factors that restrict water availability. The world′s useable water resources make up around 0.3% of the total [1].

In order to manage global water concerns, it is imperative to comprehend the availability, quality, and difficulties presented by pollution of water.

Water contamination is one of the most urgent issues of the modem world that needs immediate attention [2], [3]. The main source of water pollution is the water stream generated by the industries. The wastewater stream is composed of both organic matter and toxic metals. Among these hazardous heavy metals, that cause considerable worry are Cd(II), Pb(II), Zn(II), Hg(II), As(II), Ni(II), Cr(II), and Cu(II) [4].

Most of these metallic are toxic, carcinogenic, non-biodegradable, and may cause serious damage to the environment. Therefore, the elimination of these toxic metals from the industrial waste streams is becoming is mandatory.

Several methods are known in the literatures for the removal of heavy metals from the wastewater stream, examples on these are chemical oxidation [5], adsorption [6]–[9] , ion exchange [10], [11] membrane biological treatment, filtration [12], and others [9], [11], [13]. So far, the most acceptable technique for metal removal is the adsorption since it is easy to function and showed the highest adsorption efficiency at lowest cost. Unlimited number of materials that are natural based and synthetic were evaluated as adsorbent for heavy metals such as activated carbon [14], magnetic nanoparticles [15]–[17], chitosan [18], and others [19]–[22].

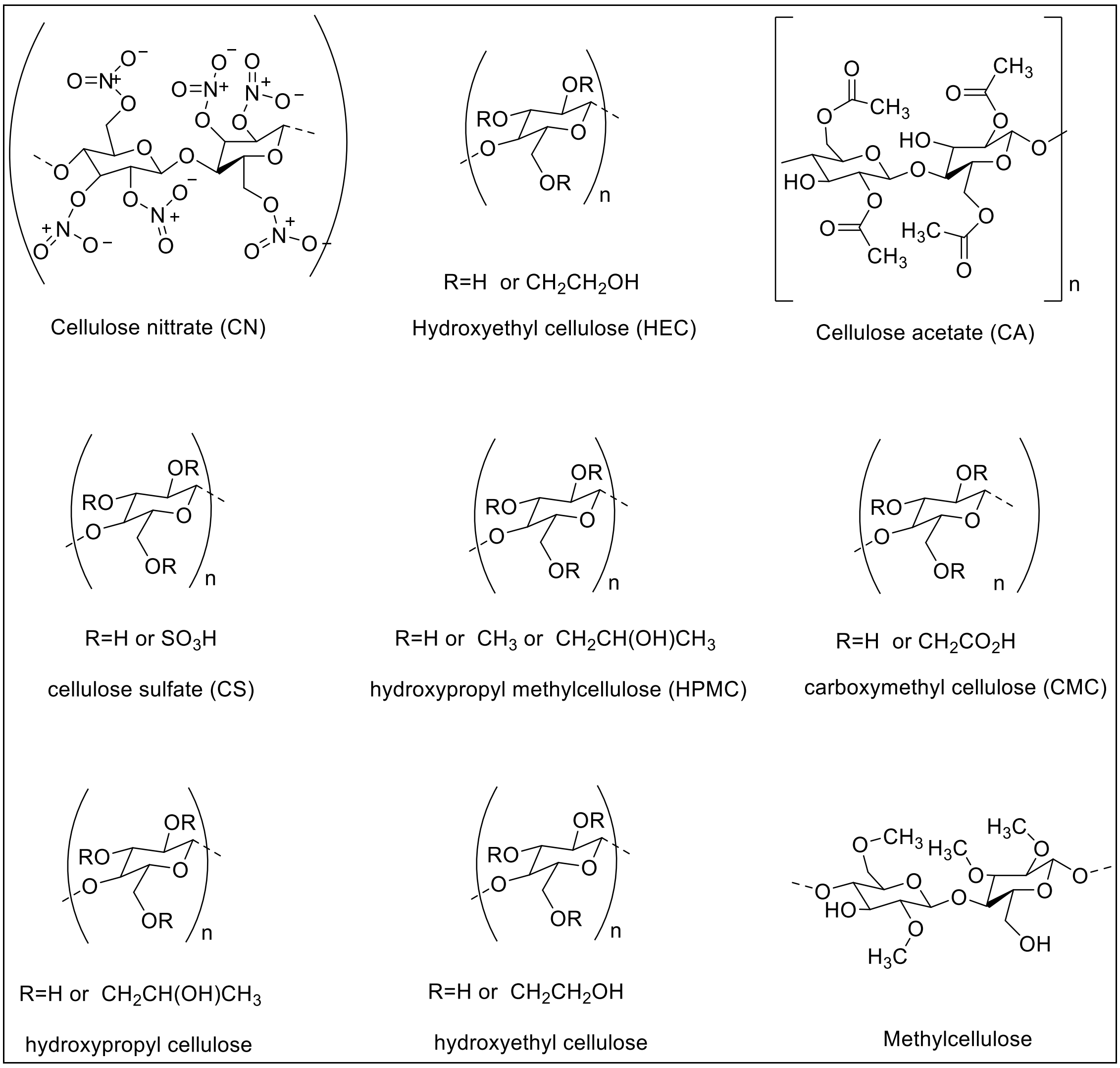
Among the other materials that were evaluated for adsorption of toxic metals from water are cellulose and cellulose composites [23], [24].

Despite some adsorbents showed high adsorption efficiency for heavy metals from aqueous phase a need still exists for an adsorbent that is selective, safe, natural based, and readily available.

Cellulose and its derivatives examples are shown in Figure 1.1 from left to right: cellulose nitrate (CN), hydroxyethyl cellulose (HEC), cellulose acetate (CA), cellulose sulfate (CS), hydroxypropyl methylcellulose (HPMC), carboxymethyl cellulose (CMC), hydroxypropyl cellulose, hydroxyethyl cellulose, and Methylcellulose [25] attracted the attention of many scientists since they possess properties that made them useful in a wide range of applications. They are renewable, biodegradable, biocompatible and available at relatively low cost.

Figure 1.1

Examples of Cellulose derivatives



Cellulose nittrate (CN)

R=H or CH_2CH_2OH

Hydroxyethyl cellulose (HEC)

Cellulose acetate (CA)

R=H or SO_3H

cellulose sulfate (CS)

R=H or CH_3 or $CH_2CH(OH)CH_3$

hydroxypropyl methylcellulose (HPMC)

R=H or CH_2CO_2H

carboxymethyl cellulose (CMC)

R=H or $CH_2CH(OH)CH_3$

hydroxypropyl cellulose

R=H or CH_2CH_2OH

hydroxyethyl cellulose

Methylcellulose

Cellulose and other renewable materials derived from agricultural waste materials, for the reasons mentioned before [26]. Among the natural based adsorbent that received the highest attention are cellulose, lignin, chitosan and hemicellulose.

Adsorbents based on cellulose, particularly those derived from waste materials like wheat straw [27], rice husk [28], kenaf [29], wood sawdust [30], and cotton linters [31], have been studied for their ability to adsorb different metal ions. There have also been reports of heavy metal removal using cellulose, the removal of Cd(II), Cu(II), and Pb (II) by using cellulose graft copolymers [32], utilizing cellulose nanoparticles to remove arsenic [33].

Carboxymethyl cellulose (CMC) is promising cellulose derivative with a diverse spectrum of sources [34]. It might be utilized as a flocculant to remediate wastewater involving hazardous metal ions, because of its abundant carboxyl and hydroxyl groups, which can form stable complex with various metal ions [35] and is capable of absorbing cation dyes [36].

CMC is distinguished by its cost-effective, biocompatible, biodegradable, and environmental friendliness, among other attributes [37]. On the other hand, CMC is water soluble with weak mechanical qualities, and the adsorption rate for metal ions and dyes is rather sluggish [38]. Furthermore, the separation process following adsorption is difficult, time-consuming, and imperfect, direct treatment of wastewater is frequently ineffective [39].

Polyurethane foam (PUF) is one of various adsorbents that shown outstanding adsorption capabilities due to its resistance to pH change, resilient porous structure, easy method of preparation, low cost, high thermal stability, large surface area, and great stability in organic and aqueous solvents [40]–[42]. All of these characteristics make foams ideal for use as an adsorbent or carrier in wastewater treatment.

Utilizing modified PUF as a CMC carrier not just makes the adsorbent easier to separate and recover, but it is additionally significantly improves the adsorption capability of micro contaminants.

In this study, hexamethylene diisocyanate, and phenylene diisocyanate were utilized as raw materials, and a solution of sodium carboxymethyl cellulose (CMC) added to each of them. Two polyurethane foams bonded with CMC were prepared. The chemical structure CMC-HMPUF and CMC-PPUF were characterized and observed by Fourier-transform infrared (FT-IR) spectrophotometer. The morphology and microstructure were examined using scanning electron microsopy (SEM). In addition, the adsorption behavior of Pb (II) of CMC-HMPUF and CMC-PPUF in water was investigated.

1.2 Water pollutants

Water is essential for all living species, and it is regarded as the world′s most valuable resource. Pollution of water is one of the most pressing issues that humans confront in their daily lives.

Water pollutants are substance that when introduced into bodies of water can change the chemical, physical, or biological qualities of the water and have a detrimental influence on the human health and environment. These contaminants can come from a variety of sources, naturally, or commercial, agricultural, industrial and domestic activities. The most frequent types of water contaminants, such as particles, both inorganic and organic, biphenyls, pesticides, surfactants, metals, phenolic resins, dyes, toxins, detergents, hormones and pharmaceuticals or another hazardous substances [43]–[45].

Pollutants have the tendency to bio-accumulate and bio-magnify owing to their high chemical stability, high toxicity, poor biodegradability, and bio-recalcitrant nature, which causes a variety of environmental issues [46].

One of the primary challenges that researchers must solve in the twenty-first century is the removal or reduction of pollutants from water, in order to improve water quality and lessen the repercussions on human and environmental health [47].

1.3 Heavy metals and toxicity

The chemical periodic table has a notable percentage of heavy metals with atomic weight (at-wt.) between 63.5 and 200.6 and density more than 5.0 g/cm^3 [48], that are hazardous at low quantities. Examples include arsenic (As), cadmium (Cd), platinum (Pt), chromium (Cr), nickel (Ni), zinc (Zn), mercury (Hg), selenium (Se), and lead (Pb).

Heavy metals can be emitted by both anthropogenic, and natural processes that end up in several parts of the environment (air, soil, water). Among the natural sources are soil erosion, volcanic eruptions, geological weathering and reactions with metal-containing rocks that are often found in the environment [49].

Anthropogenic heavy metal pathways such wastewater, pesticides, electroplating industry, textile industry, mining, paper manufacturing, tanning industry, electrolysis applications, petrochemicals, agricultural, and wastewater have been witnessed to exceed natural fluxes for certain metals [50].

These metals exposure from a variety of sources, such as polluted water, soil, food, air, and occupational settings, can prove harmful to the health of humans and other living things. These risks stem from these non-biodegradable [51], metals′ toxicity and tendency to build in the body over time. For example, exposure to cadmium and mercury can cause kidney and lung damage respectively [52]. while chromium exposure can increase the risk of some malignancies, including testicular, bladder, lung, larynx, bone, kidney, and thyroid cancer [53]. Endocrine – disrupting due to exposure (silver, copper, zinc, selenium). Acute arsenic exposure may give rise to severe disturbances of the cardiovascular, central nervous systems, and can cause cancer of lungs, bladder, and liver [54]. Also promotes a variety of skin diseases, including skin cancer, hyperpigmentation, and hyperkeratosis [55], [56].

Excessive zinc can lead to serious health issues including stomach pains, vomiting, nausea, skin irritations, and anemia [57]. Too much copper consumption causes major toxicological issues such as cramping, vomiting, seizures, and even death [58]. Nickel levels beyond the critical the reshod can cause major renal and lung difficulties, as well as gastrointestinal upset, pulmonary fibrosis, and skin rashes [59]. Mercury is a neurotoxic that can induce central nervous system damage, high mercury concentrations damage pulmonary and renal function [60].

Moreover, Heavy metals have contaminated around 40% of the world's lakes and rivers [61]. Several methods are known in the literature for the removal of Heavy metals, examples on these are: ion exchange [62], electrocoagulation [63], nanofiltration [64], adsorption [65], [66], membrane separation [67], reverse osmosis [68], [69], solvent extraction [70], [71], ultrafiltration [72], coagulation [73], chemical precipitation [74], coprecipitation [75], flotation[76], flocculation and other [77]. So far, the most acceptable technique for heavy metals (HMS) removal is the adsorption, since it is easy to function and shoed the highest adsorption efficiency at lowest cost.

1.3.1 Lead

Lead (Pb) is a common toxic heavy metal with an atomic number of 82.00 and an atomic mass of 207.20, it is bluish-gray in color. Lead has several oxidation states, the most prevalent of which are +2 and +4. Divalent states are more stable. Historically, lead was used to improve the octane rating of gasoline. Furthermore, it is one among the earliest heavy metals used in dies, pesticides, ceramic glazes, and hair [78]. Lead is widely used in a variety of industrial processes, including printing, electroplating, and the manufacturing of paints, dyes, and batteries [79]. However, lead is also exceedingly hazardous. According to WHO, the permitted amount of lead is 0.05 mg [80], and exposure to excessive levels can cause serious health consequences such as anemia, vomiting, brain damage, anorexia, and illness of the nerve and circulatory systems [81]. As a result, removing Pb (II) ions from water is critical.

1.4 Wastewater

Fresh water availability is dwindling by the day. This situation is deteriorating over time, and among the main reasons ate swift expanding populations, industrialization, increased use of pesticides in the agricultural sector, shortage of proper waste treatment processes, and a failure to enact water management strategies.

Wastewater has been identified as one of the primary sources of aquatic contamination. Wastewater is descry bed as a mix of liquid or water-carried waste evacuated from houses, industrial and commercial enterprises, as well as surface water, ground water, and storm water. Wastewater from various sources comprises a wide range of contaminants, including both organic and inorganic substances such as harmful metals, nutrients, dyes, and organic micro pollutants [82]. Globally, about 380 billion m^3 of municipal wastewater is created, with this figure expected to rise by 24% by 2030 and 51% by 2050 [83].

The release of untreated wastewater into bodies of water without any treatment procedures causes a number of environmental issues, including: Untreated wastewater typically has a high concentration of pathogenic microorganisms, hazardous substances that can live in the human digestive system and endanger human health. Moreover, untreated wastewater involving a substantial amount of organic matter will be a rise in biological oxygen demand (BOD), ammonia, and a decrease in dissolved oxygen necessary by aquatic life. Also, the degradation of organic molecules in wastewater can result in the generation of enormous amounts of foul-smelling gasses [84].

As a result, wastewater treatment is required prior it gets into bodies of water. Various chemical and physical treatment techniques are used for wastewater treatment, including as chemical precipitation, ion exchange, flocculation, adsorption, coagulation, reverse osmosis, biological degradation, etc.

This research will focus on the use of adsorption technology in the treatment of wastewater.

1.5 Adsorption

Adsorption is a valuable method for improving water quality, and one of the most effective strategies for removing a wide range of pollutants from water, including organic, inorganic substances, heavy metals, and other pollutants. It entails the adhesion of pollutants to the surface of a solid substance known as the adsorbent. Adsorbent ought to have a number of desired characteristics, such as a strong mechanical strength, specific significant surface area, inexpensive, excellent thermal stability, simple to produce in large quantities, and processing that are ecologically friendly [85]. Additionally, the sorbent must be reusable. The choice of adsorbent depends on the specific pollutants targeted and the desired treatment outcome.

Adsorption can be classed as either physical or chemisorption. The adsorbate adheres to the surface by fragile van der Waals forces, electrostatic attraction, or hydrogen bonding in the case of physisorption. Physical adsorption is reversible process, with minimal interaction energy (less than 15-30 kJ⁄mol). In the case of chemisorption, is caused by chemical interaction between adsorbate and surface locations via covalent bonds. The recent chemical bonds produced between both adsorbates and adsorbents are irreversible, have significant energy, and can range from 10 to 100 0f kJ ⁄mol [86] [87].

There are multiple parameters that influence sorption [88][89], this includes the concentration of adsorbate, the adsorbent dosage, the intrinsic qualities of the materials also very crucial like as defined surface area, particle size, hydrophobicity, functional groups present, porosity, polarity. Moreover, the experimental procedure such as method of mixing, stirring speed, contact time play a significant role. Also the temperature, ionic strength and pH [90].

Adsorption offers several advantages in water treatment, among its advantages we can highlight a versatility can target a wide range of contaminants, simple operation, a high removal capacity, relatively low energy consumption, ease of regeneration, relatively inexpensive operation and wide selection of a adsorbents. Many examples of adsorbents for waste water treatment have been reported in the literature to remove toxic pollutants as colourants and heavy metals that they include commercially adsorbents (e.g. graphene [91], activated carbon [92], and carbon nanotube [93]). Natural materials (e.g. clay [94], zeolites [95], siliceous materials [96]), bio-adsorbents (chitins and chitosan) [97], peat [98], yeasts [99], fungal biomass [100]), or bacterial biomass, agriculture, animal and industrial waste or byproducts. Among the other materials that were evaluated for adsorption of heavy metals from water are polyurethane based CMC composite.

Research and technical improvements continue to broaden the spectrum of adsorbents available and enhance the effectiveness of adsorption procedures in water treatment.

1.5.1 Polyurethanes

Polyurethanes are one of the most significant types of specialized polymers that were invented in 1937 by Otto Bayer and colleagues in Germany [101], [102], which including urethane linkage created by the polycondensation reaction between an isocyanate and a material with a hydroxyl functionality, such as a polyol or diol as shown in Figure 1.2 Appendix A.

The polyurethane building components (isocyanate and polyol) define the ultimate qualities of the product, or given it special features as hardness, flexibility, or softness. Polyols with a longer chain length provide a more flexible polyurethane. At the same time, the isocyanates rule the hard portions. This mix of soft and hard segments provides polyurethane its feature of being very versatile and useful for a wide range of applications.

The reactivity of diisocyanate is controlled by its chemical structure. Aliphatic isocyanates have a lower reactivity than aromatic ones. The existence of electron donors group on the isocyanate molecule reduces reactivity, whereas branching and bulky groups slow down the reaction due to strike hindrance. The addition of electron-drawing group on isocyanate molecules, on the other hand, might result in a quicker reaction.

Polyurethanes can be manufactured depending on the needed qualities as stiff, flexible foams, sealants, adhesives, binders, coatings, elastomers, and paints.

Polyurethane has several advantages, including the ability to keep high effect strength at lower temperatures, being easily foamable, low cost, high stability, simple to separate and repurpose, and being resistant to tear propagation, abrasion, oxidation, ozone, humidity, and fungi.

Because of their distinctive characteristics, PUF is widely employed in a variety of industries, including building, construction, furniture, refrigerator insulation, Marine applications[103], [104], footwear industries, electronics, coating[105]–[108]. Apparels [109], [110], wood composite [111], [112], and biomedical applications [113], [114].

Several recent studies addressed the possibilities of employing PU as an adsorbent for organic waste, harmful metal ion and as an oil adsorbent [115], [116]. Certain PU shown outstanding adsorption capabilities due to its low cost, resistance to pH change, large surface area, and great stability in organic and aqueous solvents[117], [118].

All of these characteristics make PU foams ideal for use as an adsorbent or carrier in waste water treatment instead of numerous more costly and inefficient adsorbents [119], [120].

1.5.2 CMC

Cellulose and its derivatives attracted the attention of many scientists since they possess properties that made them useful in a wide range of applications. They are renewable, biodegradable, biocompatible and available at relatively low cost.

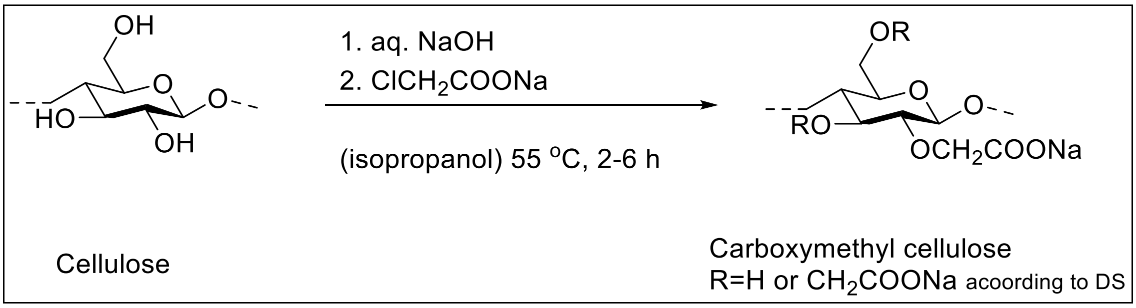
Cellulose and other renewable materials derived from agricultural waste materials [121], have been considered attractive alternatives for wastewater purification [122], for the reasons mentioned before. Among the natural based adsorbents that received the highest attention are cellulose, lignin, chitosan, and hemicellulose. Cellulosic-based adsorbents, especially those obtained from waste such as Kenaf, cotton linters, wheat straw, wood sawdust, and rice husk were already investigated as adsorption of various metal ions.

CMC is cellulose's first and main ionic derivative, a very hydrophilic polymer it has an ample super absorbing that first appeared in the 1920 s, and it's the most abundant organic compound on planet [123].

CMC is created by reacting cellulose with monochloroacetic acid, which results to introduce carboxymethyl groups onto the cellulose backbone, by replacement hydroxyl groups at carbon number 2, 3, and 6 of glucose residues with carboxymethyl groups, with a slightly stronger replacement at carbon number 2. Figure 1.3 illustrates the production of CMC from cellulose [124], [125].

Figure 1.3

Production of CMC from cellulose



Due to its distinct properties such as low cost, non- toxicity [126], high chemical reactivity, stability, water solubility [127], [128], biodegradability [129], bio adhesivity and biocompatibility. It a additionally has no known negative impacts on people′s health [130].

CMC can be used in a variety area, including in the biomedical field [131], pharmaceutical, textile [132], construction food, plastic, cosmetics [133], and oil industries. In addition, CMC is used in tissue engineering [134], bone- tissue engineering [135] and wound dressing.

On top of that, the carboxylic acid group in CMC has the capacity to absorb cationic dyes like methylene blue (MB) and establish significant electrostatic interaction with them [136]. Also, the molecule′s abundant carboxyl and hydroxyl groups may form stable complex with various metal ions, and it offers active sites for absorbing contaminants [137]. As a result, CMC blended with PUF is chosen for this study to act as adsorbent to remediate waste water involving toxic metallic ions [138], [139].

Li Wang and his colleagues prepared a variety of polyurethane porous hydrogels (PUF-s) loaded with various sodium carboxymethyl cellulose (CMC) by using a one-step foaming process; the maximum adsorption capacity of CMC-PUF-10 for MB is 27.5 mg/g [140]. Huie Liu and his team used the easy scaling- up process (i.e. wet spinning ambient pressure drying method) to create (CMC/GAs) carboxymethyl cellulose/ graphene composite aerogel bread, CMC / Gas-30 has a maximal adsorption capacity of 222.72 mg/g for MB [141].

Yashi and his coworkers used simple thermal cross-linking to create a biological adsorbent (CMC-PAA) composed of sodium carboxymethyl cellulose (CMC-PAMA), PAM, and PAA. CMC-PAA exhibited considerable MB adsorption (1611, 4 mg/g) [142].

1.6 Palestine's water pollution and water sector difficulties

The escalating water crisis in the Middle East (ME) is one of the most substantial and deadly conflicts confronting the area today. In terms of Palestine, as a vital part of the ME region, the topic of water is extremely delicate and critical. Not only are Palestinian water resources limited, constantly threatened by severe degradation, depletion, drought, and pollution, but additionally, the Israeli Occupation controls and expropriates all significant water supplies. This prevents resource usage, infrastructure upkeep, and development.

1.7 Scope of This Study

The general objective of this work is to synthesize CMC polyurethane foam with ionic functionality and use it as an adsorbent for hazardous metal ions present in industrial streams of wastewater and other polluted water.

The sup objectives include:

1. Develop a chemical method for bonding 1, 4-phenylene diisocyanate and 1, 6-hexamethylene diisocyanate to the cellulose carboxymethyl group for making novel polymers with ionic functional groups CMC-PPUF and CMC-HMPUF.
2. Characterize the new CMC-based polyurethane adsorbent by various spectroscopic techniques.

3. Determine the polymer′s optimal adsorption efficiency by investigating the influence of various factors like metal ion concentration, solution temperature, solution pH, and mixing time based on temperature.
4. Evaluate the efficiency of prepared polymer as an adsorbent for a metal ion present in wastewater.
5. Study the mechanism of adsorption, by determining adsorption kinetics and thermodynamics.

Chapter Two

Experimental Part

2.1 Materials

The chemicals and reagents that were used in this study, Carboxy-methylcellulose (CMC), N,N-dimethylacetamide anhydrous (DMAc), diisopropyl amine, 1,6-hexamethyle diisocyanate, lead (II) nitrate, 1,4-phenylene diisocyanate) were purchased from the Sigma-Aldrich Chemical Company and used with no any additional purification. All experiments were accomplished using deionized water.

2.2 Instrumentation

Several devices were utilized in this research, including FT-IR Spectrometer (Nicolet 6700.00, iD3 ATR, USA, Thermo Fisher Scientific), balance (Oahu's corp, item No AR 3130). Mass Spectrometer ICP-MS (ICE 3xxx C113500021 v1.30), pH meter (JENWAY, model: 3510), Shaking bath of water (Daihan Lab tech, 20.00 to 250.00 rpm Digital Speed Control), and Flame Atomic Absorption Spectrometer (ICE 3000 series serial number c11350021 AA System, Thermo Scientific).

2.3 Preparation of Poylurethane (PU) based carboxymethylcellulose (CMC)

2.3.1 Preparation of PU based CMC with hexamethylene diisocyanate (CMC-HMPUF)

A mixture of CMC (1.0g, 6.2 mmol/anhydroglucose repeat unit) was suspended in distilled water (1.0 mL) in a beaker and stirred until a clear thick gel was obtained (30 mints). DMAc (10.0 mL) was added to the gel followed by addition of catalytic amount of diisopropyl amine (5 drops). Excess amount of 1, 6-hexamethyle diisocyanate (2.0 mL, 2.1 g, 12.4 mmol) was then added to the CMC solution. The mixture was stirred at room temperature for 10 min, and then a few drops of water was added, an exothermic reaction started, and mass of foam produced. The resulting foam was washed with distilled water (100.0 mL) several times, filtered, and dried at 60°C for an hr.

2.3.2 Preparation of PU based CMC with p-phenylenediisocyanate (CMC - PPUF)

A mixture of CMC (1.0g, 6.2 mmol/anhydrogulocse repeat unit) was suspended in distilled water (1.0 mL) in a beaker and stirred until a clear thick gel was obtained (30 mins). DMAc (10.0 mL) was added to the gel followed by addition of catalytic amount of diisopropyl amine (5 drops). Excess amount of 1,4-phenylene diisocyanate (2.0 mL, 1.98g, 12.4 mmol) was then added to the CMC solution. The mixture was stirred at room temperature for 10 min, and then few drops of water was added, an exothermic reaction started, and mass of foam produced. The resulting foam was washed with distilled water (100.0 mL) several times, filtered, and dried at 60°C for an hr.

2.4 Batch Adsorption Studies

2.4.1 Preparation of Standard Solutions

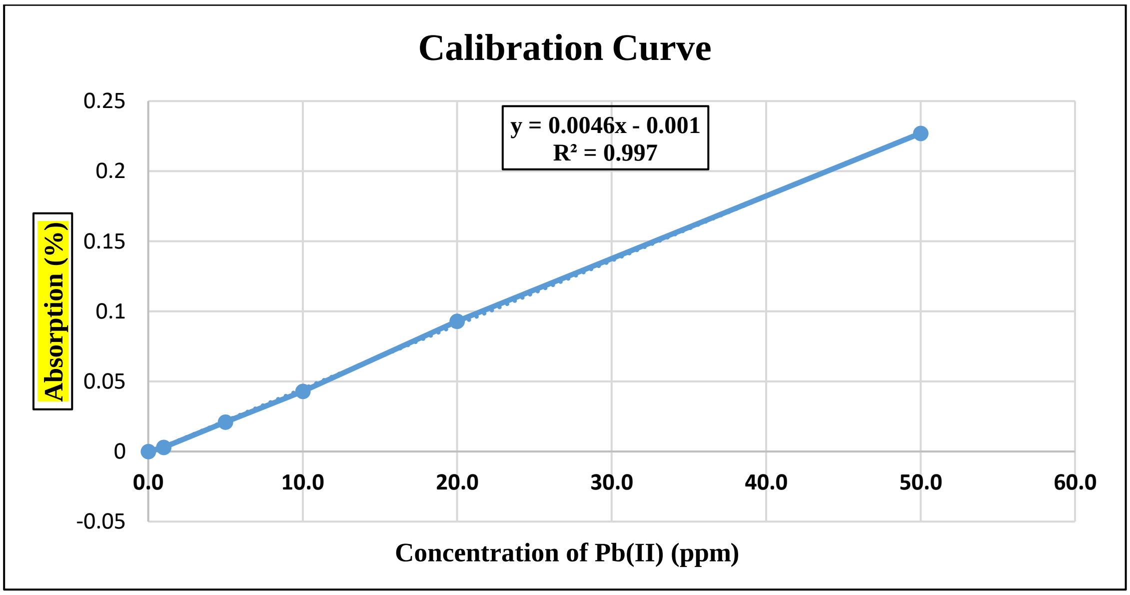
A stock solution with a concentration of a 1000 ppm of lead ion Pb(II) was prepared by dissolving 1.5985 g of lead nitrate $Pb(NO_3)_2$ in distilled water and then diluting to 1000 mL in a volumetric flask. From this solution, 5 standard solutions of Pb(II) with concentrations of 1.00, 5.00, 10.00, 20.00, and 50.00 ppm were prepared. Batch studies were conducted using standard solutions to explore the effects of the adsorbent dose, initial metal ion concentration, temperature, contact time, and pH on the effectiveness of the adsorption process.

2.4.2 Calibration curve for lead

The lead (II) ions calibration curve were generated by measuring the varied absorbance values for the provided standard solutions using the FAAS device.

Figure 2.1

The Calibration curve for Pb^{2+}



The extraction was carried out as shown in in the following steps, which included adding a particular quantity of CMC-HMPUF OR CMC-PPUF polymer to a predetermined concentration of Pb(II) solution in a glass vial, immersing in a bath of water and shaking. The samples were then filtered using a 0.45 µm syringe filter to ascertain their residual concentrations. FAAS was used to determine the concentration of lead (II).

Equations 1 and 2 were used to compute the removal percentage (%E), and equilibrium adsorption capacity (q_e) [143].

$$\%E = \left(\frac{(C_0 - C_e)}{C_0}\right) \times 100\% \text{ .... Eq. 1}$$

$$q_e = \left(\frac{(C_0 - C_e)}{m}\right) \times V \text{ .... Eq. 2}$$

Where:

q_e: the equilibrium adsorption capacity of the adsorbate (mg/g).

m: the total weight of adsorbent (g).

V: is the overall volume of pb(II) solution (L).

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

The effect of the following parameters on the metal ion extraction form waster using the prepared foams were evaluated.

2.4.3. The Impact of pH

Numerous adsorption experiments were performed out to evaluate the effect of pH on the adsorption process. For each polymer, 5 containers holding 10 ml of a 10 ppm standard solution were prepared and loaded with a 20 mg of adsorbent at 25 °C with different pH values ranging from 4.5 to 11.0. The pH levels were adjusted using 0.1 M HCl and NaOH solutions. Each sample was filtered after 30 minutes of shaking, and FAAs determined how much Pb (II) remained in each solution and summarized in the following table.

Table 2.1

Impact of pH on the adsorption of Pb^{2+} ions

CMC-	pH	Initial concentration of Pb^{2+} (ppm)	Final concentration of Pb^{2+} (ppm)	Adsorption (%)	Residual (%)	Q_e (mg/g)
HMPUF	4.5	10.0	8.33	16.69	83.31	0.83
	6.0	10.0	3.01	69.94	30.06	3.50
	7.0	10.0	0.63	93.72	6.28	4.69
	8.0	10.0	0.78	92.17	7.83	4.61
	9.0	10.0	0.89	91.07	8.93	4.55
	11.0	10.0	1.10	88.98	11.02	4.45
PPUF	3.0	10.0	5.69	43.06	65.94	2.87
	4.5	10.0	3.45	65.51	34.49	4.37
	6.0	10.0	2.32	76.80	23.20	5.12
	7.0	10.0	2.17	78.30	21.70	5.22
	9.0	10.0	2.48	75.18	24.82	5.02
	11.0	10.0	2.99	70.13	29.87	4.68

2.4.4 Impact of polymer dosage

To establish the optimal quantities of CMC-HMPUF&CMC-PPUF for lead adsorption, five Pb(II) samples (10 ml each) were generated with an optimum pH of 7 and a concentration of 10.0 ppm.

After that, polymers with known weights of 10 mg, 15 mg, 20 mg, 25 mg, and 30 mg were added to each sample. For 30 minutes, the 5 samples were mixed using a thermostat mixer set at 25 °C. The results for two polymers are reported in Table 2.2.

Table 2.2

Impact of the adsorbent dosage on the adsorption of Pb^{2+} ions

CMC-	Polymer dosage (mg)	Initial concentration of Pb^{2+} (ppm)	Final concentration of Pb^{2+} (ppm)	Adsorption (%)	Residual (%)	Q_e (mg/g)
HMPUF	10	10.0	2.56	74.38	25.62	3.72
	15	10.0	1.35	86.48	13.52	4.32
	20	10.0	0.62	93.81	6.19	4.69
	25	10.0	0.79	92.09	7.91	4.60
	30	10.0	0.83	91.67	8.33	4.58
PPUF	10	10.0	3.38	66.15	33.85	4.41
	15	10.0	2.08	79.17	20.83	5.28
	20	10.0	2.17	78.29	21.71	5.23
	25	10.0	2.36	76.45	23.56	5.10
	30	10.0	2.96	70.35	29.65	4.69

2.4.5 Contact Time impact

Effect of contact time was studied by conducting adsorption experiment for various time. For each polymer, 10 ml of 10-ppm standard solution was added to six vials at pH 7. A 20 and 15 mg for CMC-HMPUF & CMC-PPUF, respectively were added to the vials, and the resulting mixture were then put in a water bath that was shaken at desired temperature 25 ^{o}C for various times (5 to 45 min). The solutions were filtered at the end of the process, and FASS was used to measure the concentration of lead ion.

Table 2.3

Impact of the contact time on Pb^{2+} ions adsorption

CMC-	Contact time (min)	Initial concentration of Pb^{2+} (ppm)	Final concentration of Pb^{2+}(ppm)	Adsorption (%)	Residual (%)	Q_e (mg/g)
HMPUF	5	10.0	2.13	78.67	21.33	3.93
	10	10.0	1.07	89.30	10.70	4.46
	20	10.0	0.51	94.68	5.14	4.47
	30	10.0	0.65	93.94	6.51	4.67
	35	10.0	0.72	92.81	7.19	4.64
	45	10.0	0.92	90.85	9.15	4.54
PPUF	5	10.0	1.74	82.57	17.43	5.50
	10	10.0	1.57	84.29	15.71	5.62
	20	10.0	1.38	86.21	13.79	5.75
	30	10.0	2.10	78.98	21.02	5.27
	35	10.0	2.33	76.66	23.34	5.11
	45	10.0	2.47	75.28	42.72	5.02

2.4.6 The influence of adsorbate (Pb^{2+}) concentration

To identify the optimal lead ions concentration, 20.00 mg of CMC-HMPUF and 15.00 mg of CMC-PPUF polymers were added to five plastic bottles, mixed with 10ml of (5.0 ,10.0,15.0,20.0,50.0 ppm) standard solution, while keeping the other conditions for the five samples constant (pH=7, Temp = 25 °C, Time = 20 min).

Each sample was filtered, and the amount of lead ion left in solution was measured with FAAS. The outcomes are shown in Table 2.4.

Table 2.4

Impact of adsorbate concentrations on lead ions adsorption

CMC -	Initial concentration of Pb^{2+} (ppm)	Final concentration of Pb^{2+} (ppm)	Adsorption (%)	Residual (%)	Q_e (mg/g)
HMPUF	5.0	0.60	88.09	11.91	2.20
	10.0	0.53	94.67	5.33	4.73
	15.0	2.88	80.80	19.20	6.06
	20.0	5.27	73.63	26.37	7.36
	50.0	14.52	70.97	29.03	17.74
PPUF	5.0	1.37	72.66	27.34	2.42
	10.0	1.37	86.67	13.70	5.75
	15.0	2.29	80.80	15.23	8.48
	20.0	3.27	73.63	16.32	11.16
	50.0	8.50	70.97	16.99	27.67

2.4.7 Impact of temperature on adsorption percentage

To investigate how temperature impacts the adsorption process, the following procedures taken: four vials were created each one include 10 ml of 10 ppm lead standard solution and loaded with optimal dosage for the two polymers 20 mg for CMC-HMPUF & 15 mg for CMC-PPUF at pH of 7.0.

After that, the solution was agitated for 20 minutes under varied temperatures 15, 20, 30, and 40℃, and then each sample was filtered. FASS was used to determine the concentration of lead ion.

Table 2.5

Impact of temperature on the adsorption of lead ions

CMC -	Temperature (℃)	Initial concentration of Pb^{2+} (ppm)	final concentration of Pb^{2+} (ppm)	Adsorption (%)	Residual (%)	Q_e (mg/g)
HMPUF	15	10	0.99	90.07	9.93	4.50
	20	10	0.49	95.11	4.89	4.75
	30	10	0.79	92.15	7.85	4.61
	40	10	1.51	84.87	15.13	4.24
PPUF	15	10	2.25	77.53	22.47	5.81
	20	10	1.28	87.20	12.80	6.54
	30	10	1.86	81.40	18.60	6.10
	40	10	3.27	67.35	32.654	5.05

2.5 Adsorption kinetics

Adsorption kinetics offers insight on the mechanism, path, and rate controlling process of metal ion adsorption. The pseudo-first-order Eq. 3 [144] , and pseudo-second-order Eq. 4 [145] , kinetic models are the most widely used to fit experimental data [146] .

$$\ln(q_e - q_t) = lnq_e - K_1 t \text{ .... Eq. 3}$$

$$\frac{t}{q_t} = \frac{1}{(K_2 q^2)} + \left(\frac{t}{q_e}\right) \text{ .... Eq. 4}$$

In which:

qe & qt (mg/g) : the quantities adsorbate at equilibrium and time t correspondingly.

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

K_2: equilibrium constant of the second-order rate (g/mg. min).

The results should be applied to both models, and then the one with an R^2 value closer to one should be valued.

2.6 Adsorption isotherm

Understanding and evaluating the distribution of metal ions on the surface of a polymer is a crucial topic. Variety of kinetics isotherms models are used for assessing the adsorption capacity, one was a Freundlich that depicts multilayer adsorption.

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \text{ .... Eq.5}$$

Where:

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

The other was Langmuir isotherm [147][148].

$$\frac{1}{q_e} = \frac{1}{(Q_{max} K_L C_e)} + \frac{1}{Q_{max}} \text{ .... Eq.6}$$

Where;

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

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

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

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

2.7 Adsorption Thermodynamic

Changes in enthalpy (ΔH), free energy (ΔG), and entropy (ΔS), are fundamental concept in thermodynamic that play key role in predicting and describe the spontaneity and appropriateness of process.

Taken together, when (ΔH &ΔG <0), and (ΔS>0) it signifies that adsorption process release heat, also favorable and increased in random [149][150] .

The equation below summarizes the relationship between ΔH, ΔG and ΔS [151].

$$\Delta G° = \Delta H° - T\Delta S° \text{ ……………………… Eq. 7}$$

Where:

ΔS: the entropy change (J/K).

ΔG: the Gibbs free energy change (J).

ΔH: the enthalpy change (J).

The connection between (K) & (ΔG) represented by the following eq.8 [152][153] .

$$\Delta G° = -RTlnk_d \text{ (2) ……………………… Eq.8}$$

R: gas constant equals 8.314 $J.mol^{-1}. K^{-1}$

T: the absolute temperature in Kelvin.

When substitution of Eq.8 into Eq.7, both sides are divided by RT [154], [155] .

$$lnk_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \text{ ………………………… Eq. 9}$$

Where the intercept of a plot of lnk_d versus (1 /T) is equal to (ΔS°/R), and the slope is equal to is (-ΔH°/R).

2.8 Wastewater purification

To assess the effectiveness and capacity of modified poylurethane based CMC polymers to remove hazardous metal ion from water, a real sample was obtained from the Jericho sewage system. Two vials were prepared, each one filled with 10 ml of waste water, to the first vial a 20.00 mg of CMC-HMPUF polymer was added and 15 mg of CMC-PUF to the second vial. Adsorption was carried out in each vial under optimal circumstances (dose, temperature, time, and pH).

After that, the samples were analyzed using ICP-MS technique to detect the concentration of the residual metal ion in the treated sample and compare it to the bank sample.

Chapter Three

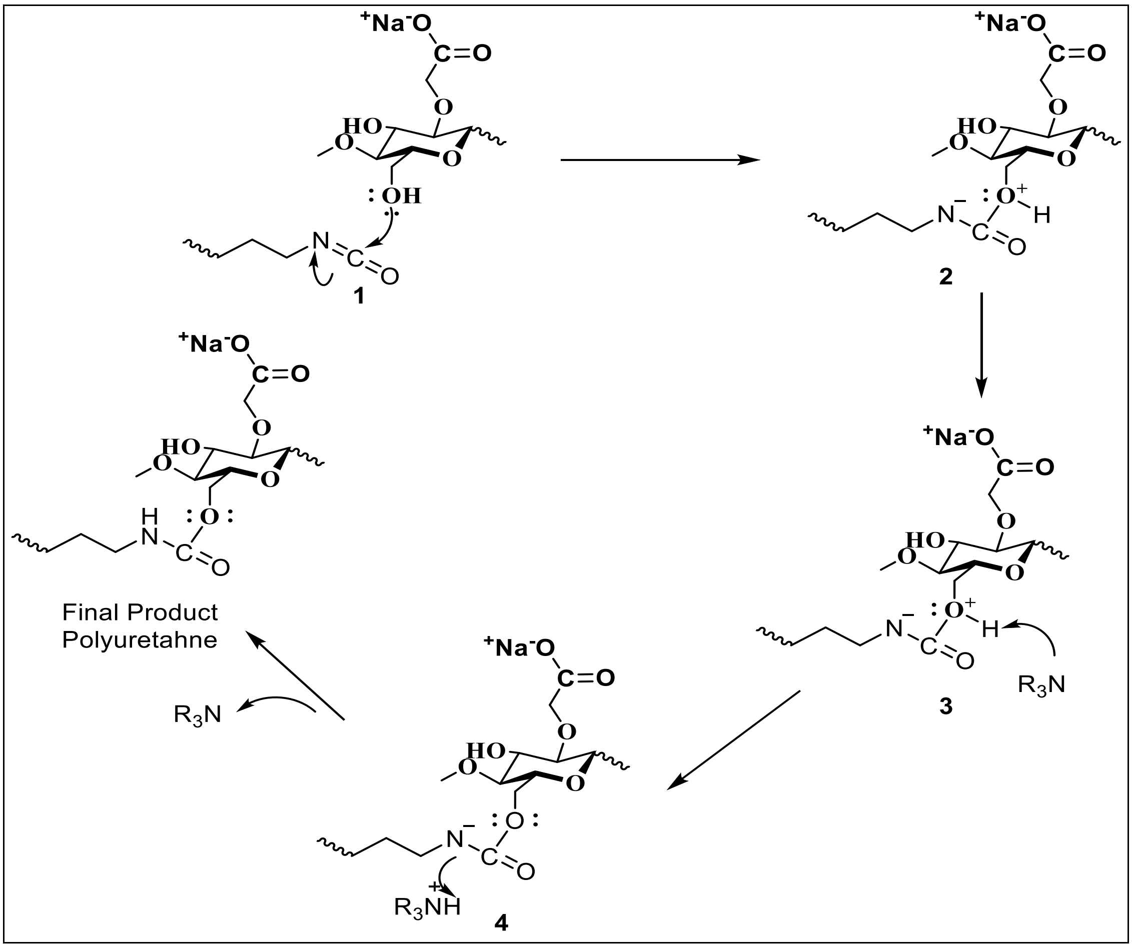
Results and Discussion

3.1 Synthesis of PU based CMC polymers

Two polymers were invented, developed, and utilized in this study to purify wastewater from hazardous metal ions. The synthesis normally involves the production of urethane linkages (–NH-CO-O-) by using diisopropylamine as a catalyst. The OH group of cellulose makes a nucleophilic attach on the isocyanate carbonyl (1), this results in the creation of new covalent connection between the nucleophilic (-OH) on the CMC and the electrophilic carbon atom of isocyanate (2). After that, the oxygen atom of the isocyanate group loses a proton to the amine catalysts (3), followed by protonation of amine anion (4) leading to a stable urethane polymer Figure 3.1.

Figure 3.1

Mechanism of polyurethane linkage forming

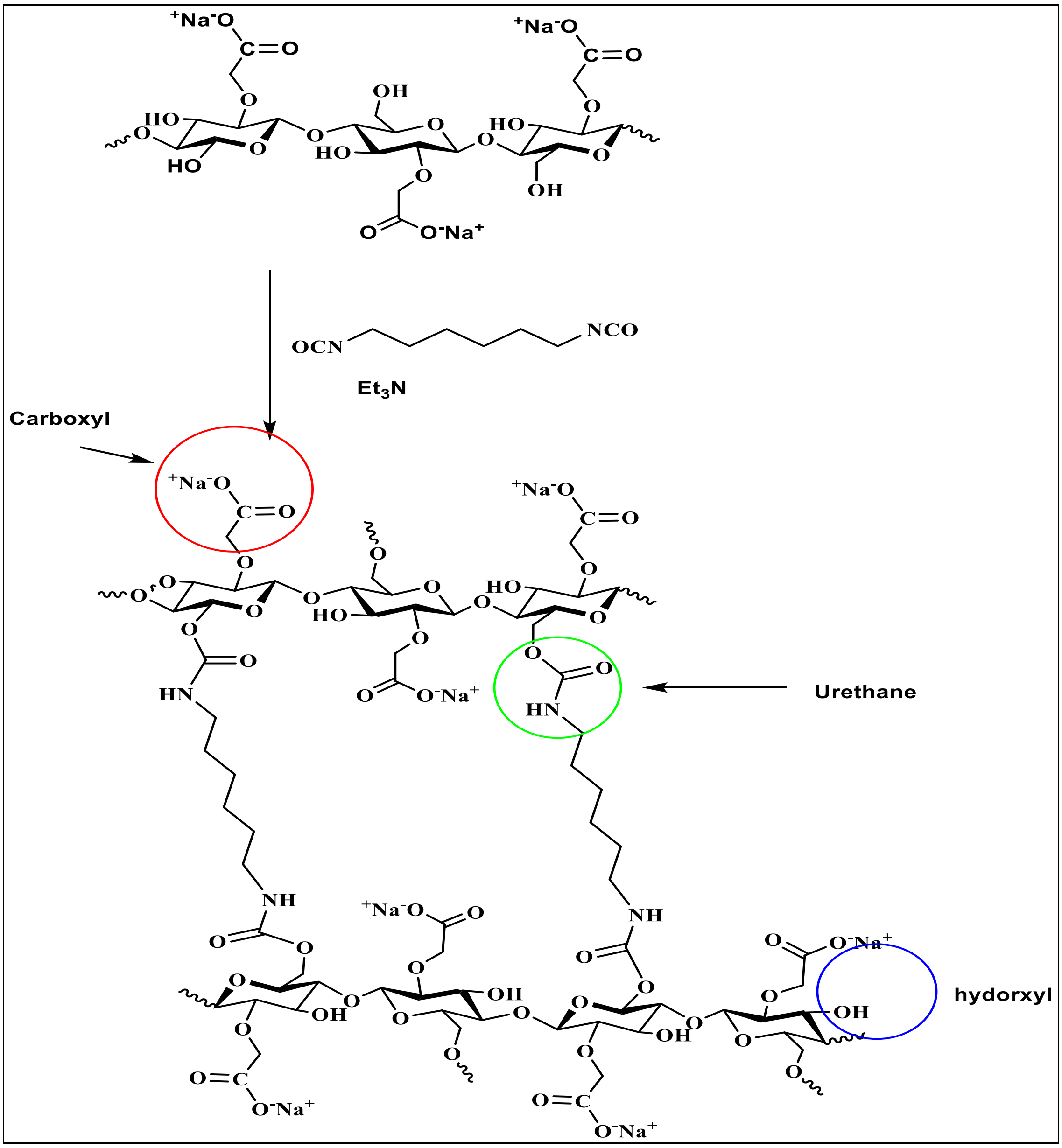


3.1.1 Synthesis of CMC-HMPUF

This polymer was synthesized form reacting carboxymethyl cellulose (CMC) with hexamethylene isocyanate in presence of catalytic amount of diisopropylaminoe shown in Figure 3.2. The produced polymer shows multiple binding sites for metal ions including carboxyl, hydroxyl, and the urethane linkage in addition to the high porosity the polymer has.

Figure 3.2

Synthesis of CMC-HMPUF



3.1.1.1 FT-IR of CMC-HMPUF

The FT-IR spectrum for CMC-HMPUF is shown in Figure 3.4 (a) Appendix A. Numerous peaks may be utilized to provide strong evidence of the presence of polyurethane foam and formation of urethane linkages, including those at 1100 cm^{-1} for C-O and 1650 cm^{-1} for C-O-NH. Peak at 3300 cm^{-1} for N-H.

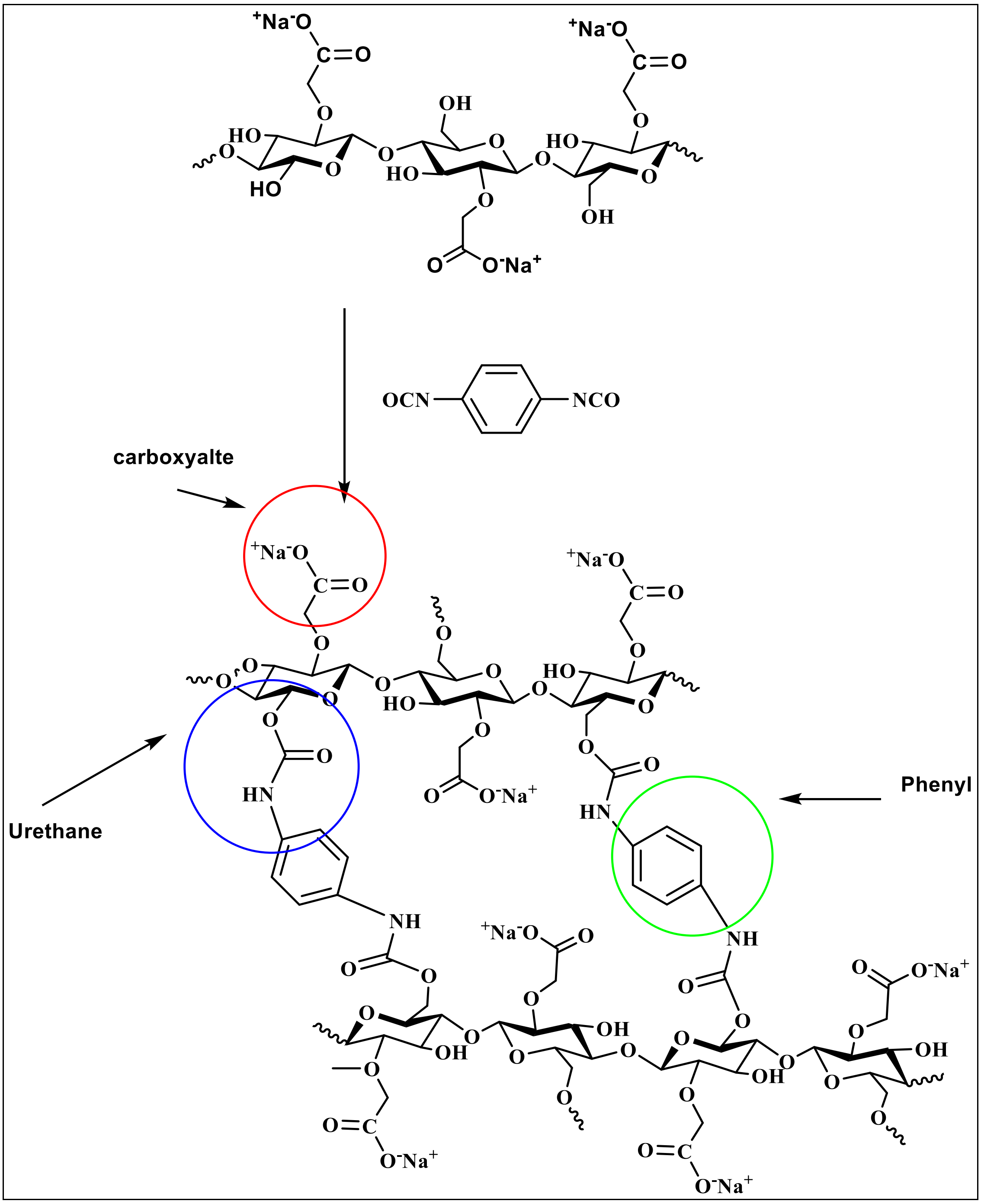
FT-IR spectrums for CMC-HMPUF shows a N-H stretching vibrations peak at approximately 3300 cm^{-1}, this corresponds to newly urethane groups established during the reaction. Peak at 1510.43 cm^{-1}, the band at 2932.96 cm^{-1} represents the C-H from methylene group, another peak at 1616.96 cm^{-1} refers to the urethane carbonyl and the 1576 peak could be attributed to the carbonyl of the carboxylate group (-COO-). The broad peak that stretches from 3300 to 220 cm^{-1} could be attributed to the OH of carboxyl group and the OH group of CMC. The peak at 1478 could be related to N-H pending.

3.1.2 Synthesis of CMC-PPUF

This polymer was created by reacting carboxymethyl cellulose (CMC) with phenylene diisocyanate as illustrated in Figure 3.3. The produced polymer shows multiple binding sites for metal ions including phenyl, carboxyl, hydroxyl, and the urethane linkage in addition to the high porosity the polymer has.

Figure 3.3

Synthesis of CMC - PPUF



3.1.2.1 FT-IR of CMC-PPUF

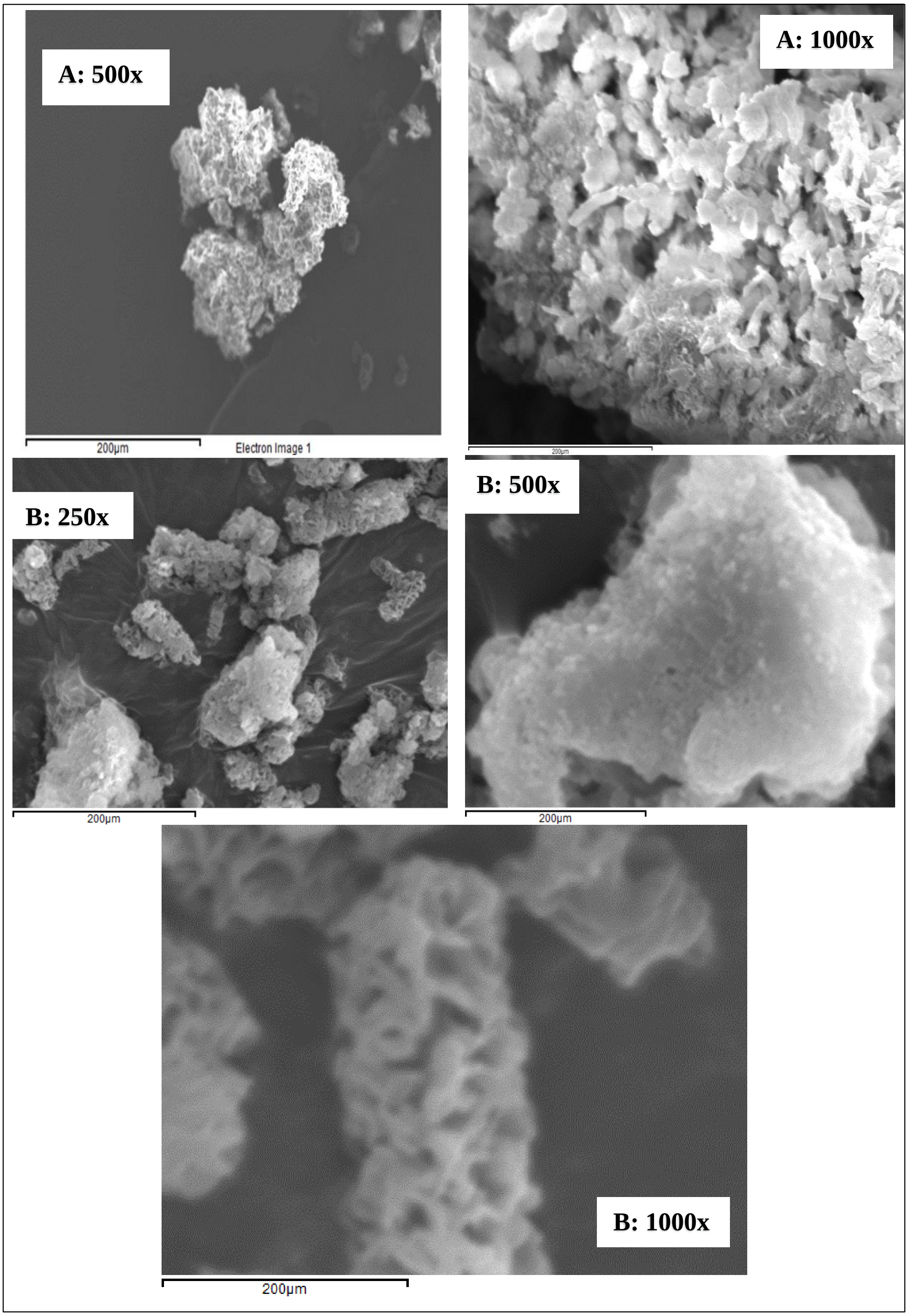
The FT-IR spectrums of CMC-PPUF are shown in 3.4 (b) Appendix A. The N-H stretching vibrations show a peak at approximately 3300 cm^{-1}; this corresponds to newly urethane groups established during the reaction. Peak at 1631.23 cm^{-1} associated with C=C aromatic ring. The band at 2932.96 cm^{-1} represents the C-H from methylene group, another peak at 1616.96 cm^{-1} refers to the urethane carbonyl and the 1576 peak could be attributed to the carbonyl of the carboxylate group (-COO-) and C=C of the phenyl ring since it appear as broad band. The peak at 1402.79 refers to the symmetric stretching, and peak at 1510 could be related to N-H pending and the broad peak that stretches from 3300 to 2220 cm^{-1} could be attributed to the OH of carboxyl group and the OH group of CMC.

3.1.3 Scanning Electronic Microscopy (SEM) Results

Images of the products obtained by SEM image of CMC-HMPUF & CMC-PPUF are shown in Figure 3.5. The images show highly porous and spongy structures for both urethanes. This could be related to the presence of polyurethane linkage. This spongy morphology makes the polymers more accessible and adds high filtering and adsorption capabilities to the prepared urethane polymers.

Figure 3.5

SEM images of a) CMC-HMPUF at 500x and 1000 x, respectively and b) CMC-PPUF at 250x, 5,000x and 10000x, respectively



3.2 Adsorption Results

The major objective of this research is to synthesize foams with high binding ability for toxic metal ions present in water and to utilize them (CMC-HMPUF & CMC-PPUF) to remove dangerous, toxic metal from wastewater. This procedure was accomplished by investigating the capacity of adsorption capabilities of the prepared polymers (CMC-HMPUF & CMC-PPUF) towards lead (II) ions. According to section 2.4.

Atomic adsorption spectroscopy was utilized to find out the remaining hazardous metal concentration in order to assess the efficacy of the adsorption process. The percentage of removal and q_e (mg/ g) the capacity for adsorption were then calculated using the eq.1 & 2 [156], [157].

3.2.1 Adsorption of Lead Ions (Pb^{2+})

3.2.1.1 Effect of pH on rate of adsorption

Adjusting and controlling the pH of metal ion solution is a crucial factor in adsorption processes, as it profoundly impacts the adsorbent's material surface and binding sites for heavy metal. For both polymers, the ideal experimental conditions were maintained (temperature 20 °C, adsorption time 20 min, 10.00 ppm solution concentration, and adsorbent dose 20.00 mg, 15 mg for CMC-HMPUF, CMC-PPUF respectively).

Figure 3.6 (a), (b) shows the results of pH value ranging from basic pH=11.0 to acidic medium pH=3.0.

From figures, 3.6 (a) and (b) The results of polymers show that metal ions were significantly eliminated at a pH of around 7.0 that is a neutral medium. In addition, the adsorption capacity rises with increasing pH until it reaches a plateau at pH = 7.0, beyond which it falls in an alkaline media. At this pH, the carboxyl group ($COO-Na^+$) is in its maximum ionic state. The greatest adsorption percentage of the first polymer HMPUF is 93.72%, while the adsorption percentage of second polymer PPUF is 78.30%.

Both polymers exhibit low adsorption in acidic medium. This might be due to polymer degradation at low pH value, or by the high concentration of H^+, thereby occupying the binding sites and competing with the metal ions. While adsorption rates decline when pH rises because of the production of hydroxyl complexes, which affects adsorption effectiveness.

3.2.1.2 Influence of Adsorbent Dosage

By altering the quantities of foams HMPUF and PPUF while maintaining constant values for metal initial concentration, pH, temperature, and contact time, the effect of adsorbent dosage on adsorption effectiveness was assessed.

The volume of the metal ion solution and the initial concentration of Pb (II) were kept at 10. 0 mL and 20.0 ppm, respectively. Adsorption occurred at 25 ^{o}C for 30 minutes. The findings are shown in Figures 3.6 (c), (d).

A crucial variable in determining removal efficiency and adsorption capacity is the dose of the absorbent (mg). It is obvious from figures 3.7 (c), and (d), that increasing the polymer dose raised heavy metal removal, and enhanced adsorption capacity until it reaches the adsorption equilibrium, which may be related to increase in available active sites on the surface of sorbent. Following that, as the dose increases, the elimination % decreases since there are reduced total accessible sites. A further possible rationale for the decline in adsorption capacity is the possibility of particle aggregation at elevated adsorbent concentrations resulting in a reduction of the adsorbent′s total surface area [158][159]. For CMC-HMPUF, the highest adsorption 93.81% was at 20.00 mg, and for CMC-PPUF, was 79.17 % at 15.00 mg.

3.2.1.3 Influence of contact time

The ideal values for pH, temperature, concentration, and dosage were constant at 7, 25°C, 10.00 ppm, and 20.00 mg for CMC-HMPUF, 15 mg for CMC-PPUF respectively, to study the influence of time on Pb (II) ions adsorption utilizing two polymer that ranged from (5-45) minutes (sec.2.4.5). Figure 3.6 (e, f) presented the results.

Another important consideration when assessing the adsorption process′s favorability is contact time.

Figures 3.6 (e), and (f) display the relation between the time and the adsorption capacity. The figure shows that the adsorption capacity of the two foams increases significantly at first before progressively declining. Adsorption ceased and achieved equilibrium after 20 minutes. The contact time that yields the lowest residual concentration of adsorbate was determined to be the ideal one. The results given in figures illustrate that highest % of removal Pb (II) ions for CMC-HMPUF and CMC-PPUF is 94.68, 86.21% respectively, and that 20.00 min is the optimum contact time for both polymers.

The adsorption capacity frequently rises fast during the first contact time due to the number of unoccupied binding sites on the adsorbent surface. The adsorption equilibrium has been reached when the growth in adsorption capacity levels off, and progressively declines. This is because there are fewer available adsorptive sites with longer contact times, which results in significantly greater resistance when the adsorbate and adsorption sites collide [160].

Given the short time required to reach adsorption equilibrium, it may be possible to treat greater treatment volumes or batches in less time, which would enhance removal efficiency and reduce the cost of wastewater treatment systems [161].

3.2.1.4 Effect of Pb (II) Initial Concentration

This carried out to examine how initial metal ion concentration influenced on the adsorption rate by prepared polymers. The optimal quantity of polymer was set at 20.00 mg, 15 mg for CMC-HMPUF& CMC-PPUF respectively. The other parameters (pH, solution volume, shaking time, temperature) were adjusted at 7, 10.00 ml, 20 minutes, 25°C sec 2.4.5. figure 3.6 presents outcomes for concentration range of 1-50 ppm.

Figure 3.6 (g, h) depicts a proportionate concentration for two polymers between adsorption performance and metal ion concentration. In the beginning, the removal capacity increases as the concentration of Pb (II) ions rises until it arrives at a plateau. This happens because high number of free adsorption sites on adsorbent surface, but after a plateau, all of the binding sites are saturated.

For both polymers, the highest percent of adsorption was 10 ppm of lead (II) solution. At this concentration, the maximum percentage of removal of ions reaches 94.67% for CMC-HMPUF and 86.67% for CMC-PPUF.

3.2.1.5 Effect of Temperature

To determine the optimal temperature for adsorption of Pb(II) ions by both adsorbents, the ideal condition for dosage, time, pH and Pb(II) concentration must be adjusted to (20.00 mg, 20 min, 10 ppm, PH 7) for CMC-HMPUF respectively, and (15.00 mg, 20 min, 10 ppm, PH 7) for CMC-PPUF respectively, as depicted in fig 3.6 (i, j).

Another crucial factor to optimizing adsorption processes is temperature, which can impact the activation energy that has a substantial affect removal rate as well as the adsorption capacity.

There are two types of adsorption processes: endothermic and exothermic. If increasing the temperature causes the adsorption to increase, then this process ought to be endothermic. If not, this ought to be an exothermic reaction [162].

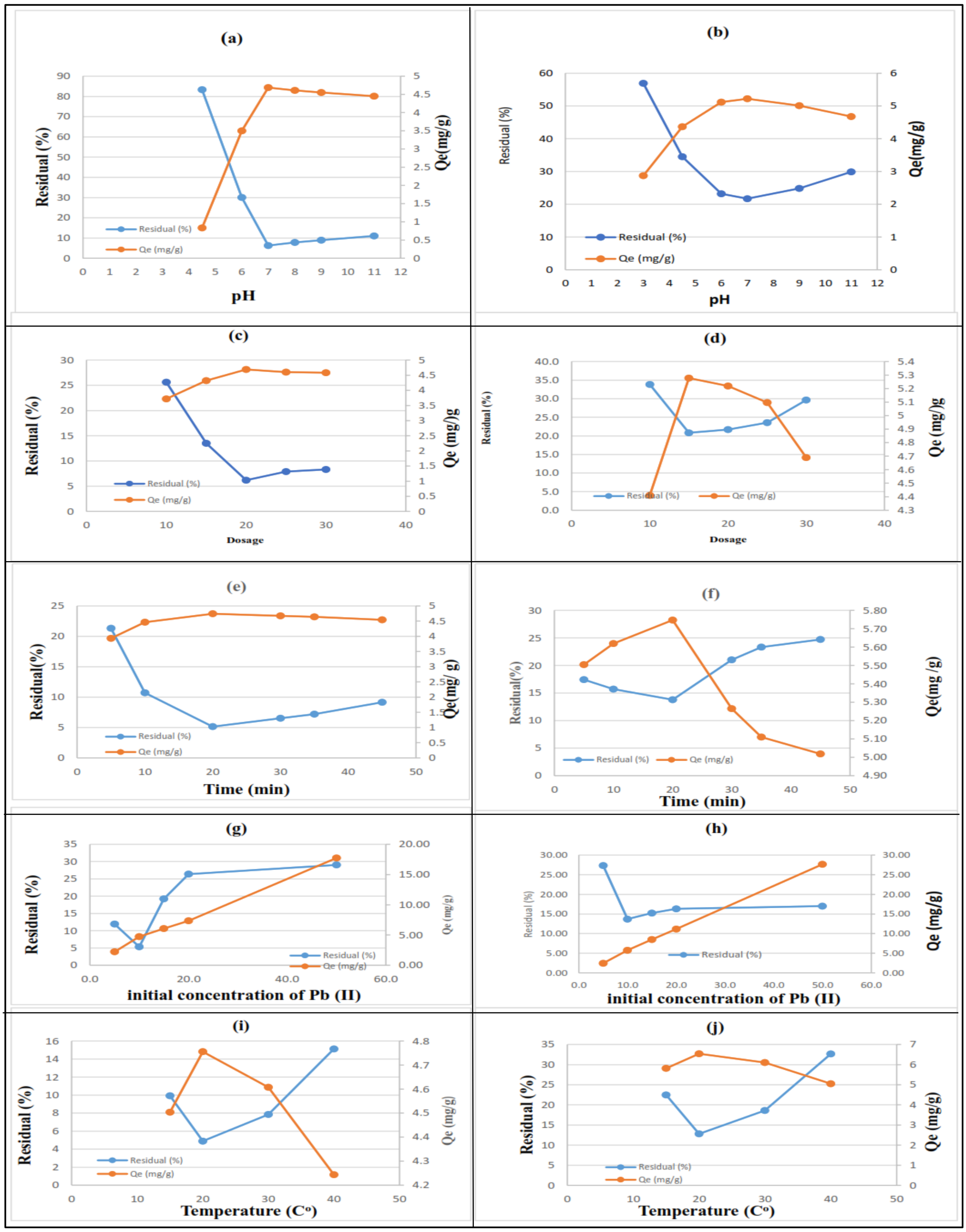
In the case of endothermic adsorption, materials adsorbed become more mobile due to increased temperature and an increase in the adsorptive forces between the active sites on the adsorbent surface and the adsorbate species. So improving process of adsorption [163].

As shown in figure 3.6 (i, j), the adsorption of Pb (II) ions using the two polymers decreased with increasing temperature. Low temperatures promote the complexation reactions of Pb (II) with polymers, however higher temperatures enhance ion solubility and increase the kinetic energy of particles on the adsorbent surface, increasing the likelihood of particle separation from the adsorbent surface [164], [165]. The 20℃ was chosen as the optimum temperature for the two polymers, with removal of 95.11% for CMC-HMPUF, and 87.20% for CMC-PPUF. The results indicate that the adsorption process of both polymers occurred spontaneously and exothermic.

However, the outcomes show a decline in adsorption capacity as temperature rises for both polymers.

Figure 3.6

Factors affecting the adsorption process



Note: (a) Effect of pH on % capacity of Pb(II) (CMC-HMPUF), (b) Effect of pH on % capacity of Pb(II) (CMC-PPUF), (c) Effect of adsorbent dose on %removal on the adsorption capacity of Pb(II) (CMC-HMPUF), (d) Effect of adsorbent dose on %removal on the adsorption capacity of Pb(II) (CMC-PPUF), (e) Adsorption capacity of Pb(II), and the significantly effect of contact time (CMC-HMPUF), (f) Adsorption capacity of Pb(II), and the significantly effect of contact time(CMC-PPUF). (g) Effect of initial adsorbate concentration (CMC-HMPUF) on the adsorption capacity of Pb(II), (h) Effect of initial adsorbate concentration (CMC - PPUF) on the adsorption capacity of Pb(II). (i) Effect of temperature on the removal capacity of Pb(II)(CMC-HMPUF), (j) Effect of temperature on the removal capacity of Pb(II) (CMC-PPUF).

3.3 Optimum adsorption parameters

The optimal adsorption results for Pb (II) ions using CMC-HMPUF or CMC-PPUF are summarized in table 3.1.

Table 3.1

Optimum Adsorption Parameters for lead ion

Adsorbent CMC -	% Adsorption	Parameters pH, Adsorbent dosage (mg), Contact time (min), concentration (ppm), Temp (°C),
HMPUF	95.11%	7, 20, 20, 10,20
PPUF	87.20%	7, 15, 20, 10, 20

3.4 Purification of wastewater by HMPUF and PPUF polymers

To assess the efficacy of the CMC-HMPUF and CMC-PPUF polymers in adsorbing hazardous heavy metal ions, both polymers were applied to an actual sample of sewage water under optimal adsorption conditions as we mentioned earlier (sec. 2.8). The concentrations of various heavy metals prior to and following polymer usage are shown in table 3.2 Appendix B.

Both polymers demonstrate good adsorption for many metal ions. Furthermore, Pb(II) displayed outstanding adsorption rates, with CMC-HMPUF polymer absorbing 93.75% of the ion, and CMC-PPUF polymer removing 87.20%.

3.5 Adsorption Isotherm

To assess the efficacy of the generated CMC based polymer in eliminating *Pb(II*) ions at equilibrium. Two mathematical models were used Freundlich (Eq.5), and Langmuir (Eq.6).

The Freundlich isotherm is a popular model for characterizing the adsorption process in multilayer heterogeneous systems. For adsorption on a monolayer homogeneous surface, the Langmuir model is preferable.

3.5.1 Langmuir adsorption isotherm

The Langmuir model rests on a number of fundamental tense are, there are a limited number of homogeneously distributed active regions across the surface of the adsorbent, monolayer adsorption and desorption on one active center have no effect on the adsorption on another active center because all active centers have the same amount of energy [166]–[168].

At equilibrium, q_e is the amount of adsorbed per unit mass of polymer (mg/g).When the graph plot of $1/q_e$ vs $1/c_e$ displays a straight line with a high R^2 value, adsorption follows this paradigm.

The isotherms shapes are indicated by the value of R_L as being irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear (RL=1), or unfavorable ($R_L > 1$).

Table 3.3

Langmuir model values

Adsorbent CMC -	Concentration (ppm) Ci	$[Pb^{2+}]$ (ppm) Ce	q_e	$1/q_e$	$1/C_e$
HMPUF	5	0.60	2.20	0.45	1.68
	10	0.53	4.73	0.21	1.87
	15	2.88	6.06	0.17	0.35
	20	5.27	7.36	0.14	0.19
	50	14.52	17.74	0.06	0.07
PPUF	5	1.37	2.42	0.41	0.73
	10	1.37	5.75	0.17	0.72
	15	2.29	8.48	0.12	0.44
	20	3.27	11.16	0.09	0.31
	50	8.49	27.67	0.04	0.12

According to figure 3.7 (a) and the results in table 3.4, the R_L value for CMC-HMPUF and CMC-PPUF is in the range of ($0 < R_L < 1$), demonstrating that the adsorption is favorable for both polymers.

3.5.2 Freundlich isotherm model

The Freundlich isotherm is an empirical modal that suitable for adsorption processes occurs on heterogonous surfaces with various adsorption energies, and over many layers.

When graphing ln (q_e) vs ln (C_e) using Eq.5, which is the linearized form of the Freundlich isotherm, if the data shown an R^2 value near to 1 with a straight line, The adsorption follows this model, additionally adsorption is seen favorably if n > 1.

The log (C_e) against log (q_e) plots slope and intercept were used to determine the constants K_f and n. The parameters of the Freundlich model for the sorption of lead by two polymers based on CMC are provided in table 3.6 Appendix B.

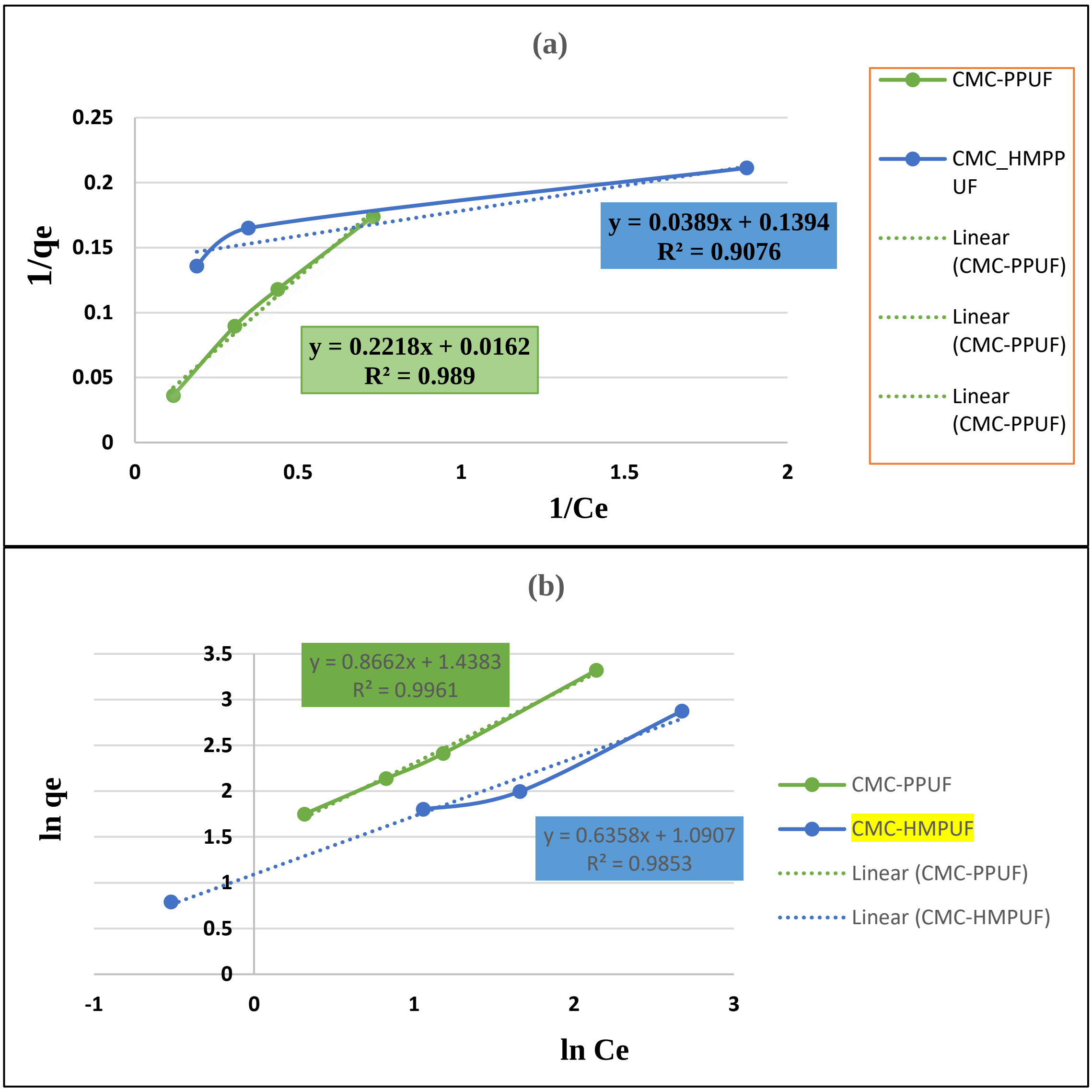
Table 3.4

Freundlich model values

Adsorbent CMC-	Concentration (ppm) C_i	[Pb^{2+}] (ppm) C_e	q_e	Ln q_e	Ln C_e
HMPUF	5	0.60	2.20	0.79	-0.52
	10	0.53	4.73	1.55	-0.63
	15	2.88	6.06	1.80	1.06
	20	5.27	7.36	2.00	1.66
	50	14.52	17.74	2.88	2.68
PPUF	5	1.37	2.42	0.88	0.31
	10	1.37	5.75	1.75	0.31
	15	2.29	8.48	2.14	0.83
	20	3.26	11.16	2.41	1.18
	50	8.49	27.67	3.32	2.14

Figure 3.7

Adsorption Isotherm



Note: a) Langmuir model for adsorption of Pb^{2+}on CMC-HMPUF, CMC-PPUF, (b) Freundlich model for adsorption of Pb^{2+} by CMC-HMPUF, CMC-PPF.

As observed in Table 3.4, 3.6 Appendix B, the correlation coefficient (R^2) for both polymers is larger and considerably closer to one for the Freundlich isothermal model than for the Langmuir isothermal model. As a result, the two adsorbents (CMC-HMPUF, CMC-PPUF) follow this model, and the adsorption process occurs not just at the surface, but also at the polymers multilayers, well as on heterogonous surfaces.

3.6 Adsorption kinetics

To explain the adsorption process of pb (II) ions, adsorption kinetics models such as the pseudo-first-order (Eq. 3) and pseudo-second-order models (Eq. 4) are utilized.

3.6.1 Pseudo-first order model

The adsorption fits this model if the graph of ln (q_e-q_t) vs time presents a straight line with a high R^2 value.

3.6.2 Pseudo-second order

Adsorption follows this model if the graph of t/q_t vs time presents a straight line with an R^2 close to 1.

Table 3.7

Values of the pseudo-first order model

Adsorbent CMC-	Time (min)	$[Pb^{2+}]$ (ppm) Ce	qt (mg/g)	ln(qe-qt)
HMPUF	5	2.13	3.93	-0.22
	10	1.07	4.46	-1.32
	20	0.54	4.72	-5.27
	30	0.65	4.67	-2.84
	35	0.72	4.64	-2.37
	45	0.92	4.54	-1.66
PPUF	5	1.74	5.50	-1.39
	10	1.57	5.62	-2.01
	20	1.38	5.75	-5.12
	30	2.10	5.27	-0.72
	35	2.33	5.11	-0.44
	45	2.47	5.02	-0.31

Table 3.8

Pseudo-second -order model values

Adsorbent CMC-	Time (min)	$[Pb^{2+}]$ (ppm) C_e	q_t (mg/g)	t/q_t
HMPUF	5	2.13	3.93	1.27
	10	1.07	4.46	2.24
	20	0.54	4.72	4.23
	30	0.65	4.67	6.42
	35	0.72	4.64	7.54
	45	0.92	4.54	9.91
PPUF	5	1.74	5.50	0.90
	10	1.57	5.62	1.78
	20	1.38	5.75	3.48
	30	2.10	5.27	5.70
	35	2.33	5.11	6.85
	45	2.47	5.02	8.97

The PFO model fitted a curve of ln (q_e-q_t) versus t, which is seen in figure 3.8 (a). The PSO model fitted a curve of t ⁄q_t and t, which is depicted in figure 3.8 (b). Correlation coefficients (R^2) are assessed to characterize how well the adsorption kinetics model applies. In both polymers, the correlation coefficients (R^2) values for the PSO were greater and near to 1 than those for the PFO. This indicates pb(II) adsorption on polymers (CMC-HMPUF&CMC-PPUF) follows PSO.

Furthermore, the theoretical q_e value for the two polymers (4.65, 4.94 mg/g) are very close to the experimental q_e (4.73, 5.75 mg/g) in PSO model, so it can be concluded that the pb (II) adsorption on the surface of the modified CMC polymers conforms to the PSO.

3.6.3 Intra-particle diffusion Weber-Morris model

In this work, the liquid film model and intra-particle diffusion model were used to study the sorption mechanism. Adsorption metal removal normally comprises numerous phases. In the initial stage involves transferring metal ions from the solution to the CMC-HMPUF, CMC-PPUF polymer′s outer surface. After that the ions diffuse across the boundary layer, then the ion can interact with active adsorption sites on the surface of the CMC-HMPUF, CMC-PPUF polymers. Finally, ion adsorption and intraparticle diffusion to the interiors site of CMC (HMPUF, PPUF) polymers particles [169][170].

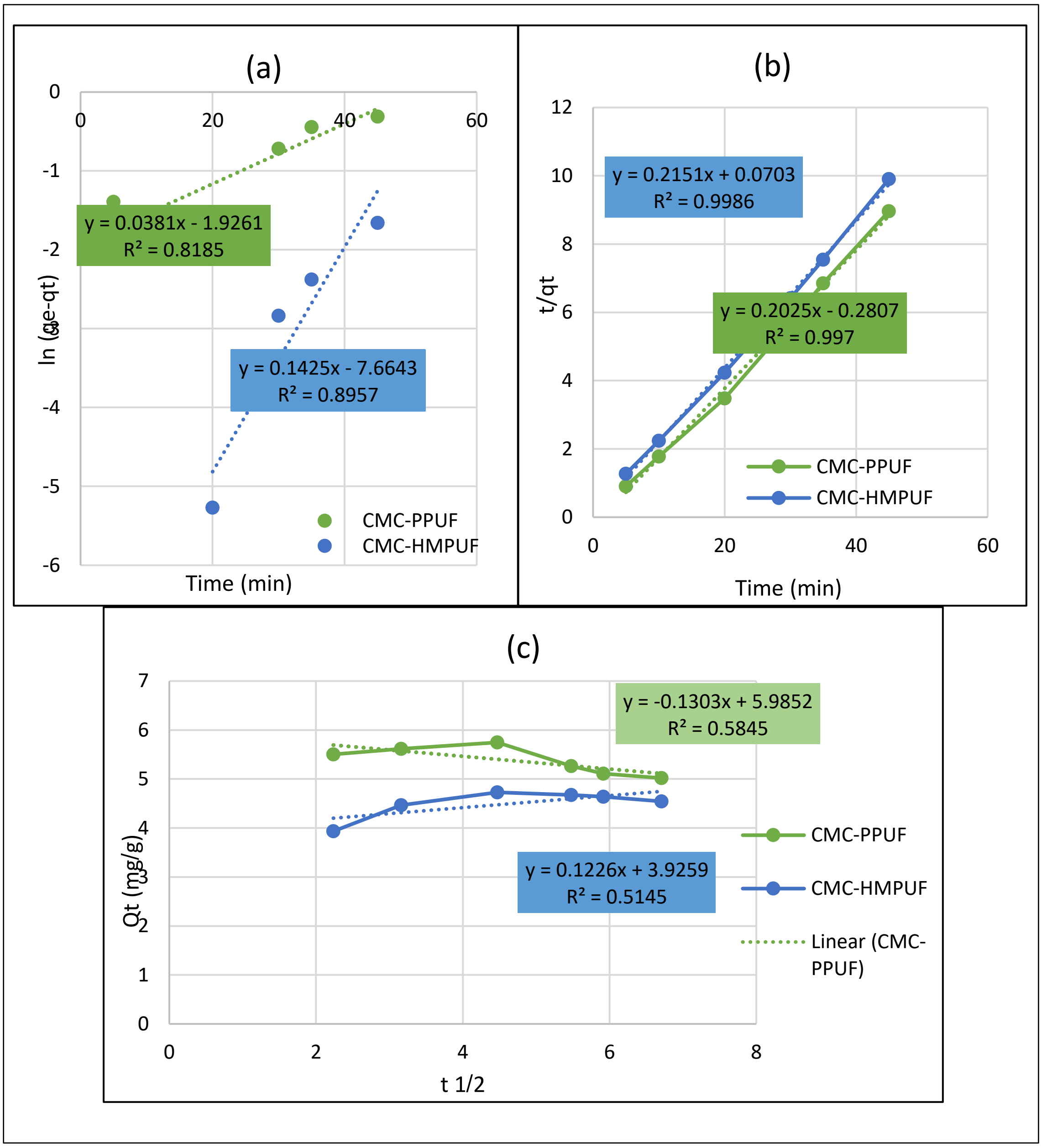
The Weber-Morris model (Eq.10) [171] is used to characterize the intraparticle diffusion mechanism, that happens during adsorption, and can give insight into whether intra-particles diffusion is a rate -controlling stage in the overall adsorption process.

$$Q_t = K_{id} t^{\frac{1}{2}} + Z \text{ ……………………….. Eq .10}$$

Where Z (mg/g) is the thickness of the boundary layer, K_{id} (mg/g $min^{1/2}$) is the intraparticle diffusion rate constant, and Q_t are adsorption capacities (mg/g) at various time (t, min).

Figure 3.8

Adsorption kinetics models on to CMC-HMPUF, and CMC-PPUF)



Note: Model of (a) Pseudo first-order, (b) Second order, and (c) Intra- particle diffusion model for the Pb (II) adsorption onto CMC-HMPUF, and CMC-PPUF.

Fig.3.8 (c) (Q_t vs. t 1/2) was used to get Z and k_{id} values. Table 3.10 (c) Appendix B summarizes the values. The values of Z demonstrate a rise in interior mass transfer potential, a decline in exterior mass transfer potential, and a broadening of the outer layer.

As seen in figure 3.8 (c), the initial sharper stage of the process is the external surface adsorption stage, also known as the immediate adsorption step; this step is missing and finished in less than 3 minutes. Stage 2 steady adsorption, often alluded to as (intraparticle diffusion), is the rate-controlled step is attained and continues from 3 min to 10 min. The rate of intraparticle diffusion starts to slow down in the last section after 10 minutes, which is the final equilibrium stage, due to decreases adsorbate concentrations in the solution.

3.6.4 Liquid film diffusion model

The liquid film diffusion model is concerned with the flow of adsorbate molecules from the bulk liquid phase to the adsorbent materials exterior surface table 3.7(d) Appendix B.

Eq.11 depicts the liquid film diffusion model.

$$ln(1 - F) = K_{fd}t \text{ .... Eq. 11}$$

Where:

F: The ratio obtained at equilibrium (F = qt/qe)

K_{fd} : The film diffusion coefficient (min^{-1}).

If the figure plot between ln (1-F) vs. t linear with intercept zero, so the diffusion across the liquid layer containing the CMC-based polymers controls the adsorption kinetics.

Figure 3.9 in Appendix A displays the findings obtained for the adsorption of Pb (II) by the CMC-HMPUF and CMC-PUF polymers to the liquid film diffusion model. The graph had a correlation value of 0.64, 0.20 for CMC-HMPUF and CMC-PPUF respectively, and no straight lines that crossed the point of origin. This demonstrates that it is not the diffusion of adsorbate via the liquid layer surrounding the CMC-HMPUF; CMC-PPUF based polymers that impacts the rate of adsorption.

When the values of the film diffusion coefficient and the intra-particle diffusion coefficient are compared for both produced polymers, the film coefficient is the lowest. Indicating that diffusion to the outside surface might represent the rate-limiting step in the adsorption process.

Throughout the adsorption process, the best correlation is provided by kinetic model PSO, whilst the intraparticle diffusion model is just suitable for the early phases of the adsorption procedure. Consequently, it was observed that intraparticle diffusion was rate limiting for CMC-HMPUF, CMC-PPUF that was followed by the PSO kinetic model.

3.7 Thermodynamics adsorption by CMC-HMPUF &CMC-PPUF

In this work, numerous thermodynamic parameters such as (S^o) entropy, (G^o) Gibbs free energy change, (H^o) enthalpy, and so on are computed to describe the adsorption process of Pb (II) ions by CMC-HMPUF, CMC-PPUF polymers, estimate its feasibility, and spontaneity.

In this study, to characterize the adsorption process of Pb(II) ions by CMC-HMPUF, CMC-PPUF polymers, predicting its feasibility and spontaneity, different thermodynamic parameters are calculated like (ΔS^o) entropy, (ΔG^o) Gibbs free energy change, (ΔH^o) enthalpy , and so on[172] .

By utilizing the Van′t Hoff plot equation. The thermodynamic parameters (ΔS^o and ΔH^o) of the absorption of lead (II) ions on (CMC-HMPUF) or (CMC-PPUF) can be calculated from graph of In K_d versus (1/T) whereas y-intercept equal of ($\Delta S^o/R$), and slope of ($-\Delta H^o/R$).

As shown in table 3.13 in Appendix B, the adsorption of Pb (II) on CMC-HMPUF and CMC-PPUF adsorbent happened spontaneously due to the fact that all ΔG^o values are less than zero (negative). Also, exothermic process consequently a cheap reaction (ΔHo<0), and spontaneous at lower temperatures (ΔSo<0), and that’s consistent with our finding that the optimal adsorption temperature is 20°C.

3.8 Conclusion

In this study, CMC-HMPUF and CMC-PPUF polymers were produced using a process devised in our laboratory by reacting known quantities of CMC with excess amounts of 1, 6-hexamethyle diisocyanate and 1, 4-phenylene diisocyanate, respectively, in the presence of diisopropyl amine as a catalyst. FT-IR was used to identify the structure of the two-produced polymers. In order to examine the best adsorption condition, contact duration, concentration, temperature, dose, and pH parameters were all examined.

The two polymers were then utilized to purify tainted wastewater under optimal value of the examined parameters for CMC-HMPUF polymer was about 10.00-ppm concentration, 20.00 mg dose, temperature of 20°C, pH value of 7, and contact time of 20.00 min. The best conditions for CMC-PPUF polymer were 10.00-ppm concentration, 15.0 mg dose, temperature 20℃, pH 7.00-, and 20.00-min contact time. For numerous elements found in a genuine sample of wastewater, the adsorption effectiveness ranged from good to exceptional. The maximum Pb removal efficiency was around 95.11% for CMC-HMPUF, and 87.20% for CMC-PPUF.

Furthermore, the reaction isotherm, kinetics, and thermodynamics were all investigated. And the findings demonstrated for two polymer that Pb(II) adsorption process is a exothermic ($\Delta H^o < 0$), Spontaneous ($\Delta G^o < 0$) . Also the results revealed that the equilibrium reaction with Pb(II) follows PSO.

3.9 Recommendations

1. The production of CMC polymers may be investigated utilizing different materials or cross- linkage agents.
2. These polymers can be studied for diverse uses in medication administration and the pharmaceutical sector.
3. Extra components can be added to the polymers to improve its absorption effectiveness.

List of Abbreviations

Abbreviations	Meaning
WHO	World Health Organization
PPCPs	pharmaceuticals and personal care products
PUF	Polyurethane foam
EPA	EPA Environmental Protection Agency
1/n	Dimensionless Freundlich constant
Z	Atomic Number
DP	Degree Of Polymerization
OISW	Olive Industry Solid Waste
CMC	Carboxy Methyl Cellulose
PU	Polyurethane
CMC-HMPUF	Carboxy methyl cellulose-based hexamethyle poylurethane
CMC-PPUF	Carboxy methyl cellulose-based phenylene poylurethane
FAAS	Flame Atomic Adsorption Spectrometer
FT-IR	Fourier-Transform Infrared Spectrophotometer
SEM	Scanning electron microscopy
DMAc	N, N-dimethylacetamide anhydrous
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
PFO	pseudo first order
PSO	pseudo second order
R^2	Correlation coefficient (regression coefficient, fitting coefficient)
HMS	Heavy metals
C_f	metal ions equilibrium Concentration in the sample solution after treatment (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_d	The thermodynamic gas constant
K_f	Freundlich constant
K_L	Langmuir isotherm constant
T	The Absolut temperature
R_L	Separation factor dimensionless constant
$\Delta S°$	The change in entropy
$\Delta H°$	The change in enthalpy
$\Delta G°$	The change in Gibbs free energy
R	The universal gas constant
K_{id}	The Intraparticle Diffusion Rate Constant
DS	Degree of substitutions
Z	The Thickness Of The Boundary Layer
K_{fd}	The Film Diffusion Coefficient

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Appendices

Appendix A

Figures

Figure 1.2

polycondensation reaction

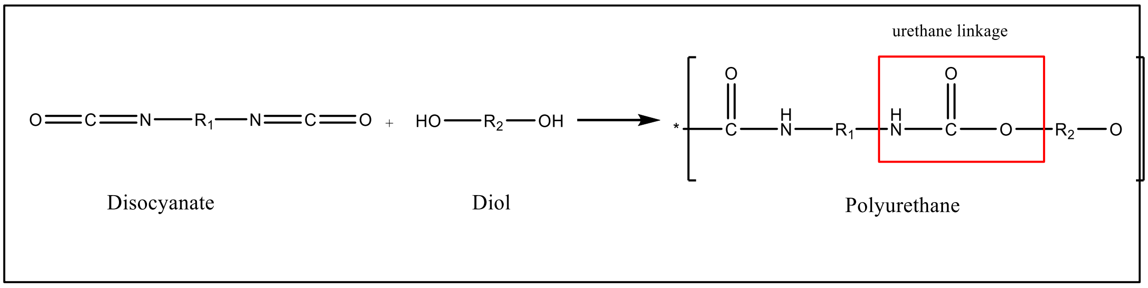


Figure 3.4 (a)

FT-IR spectra of CMC-HMPUF

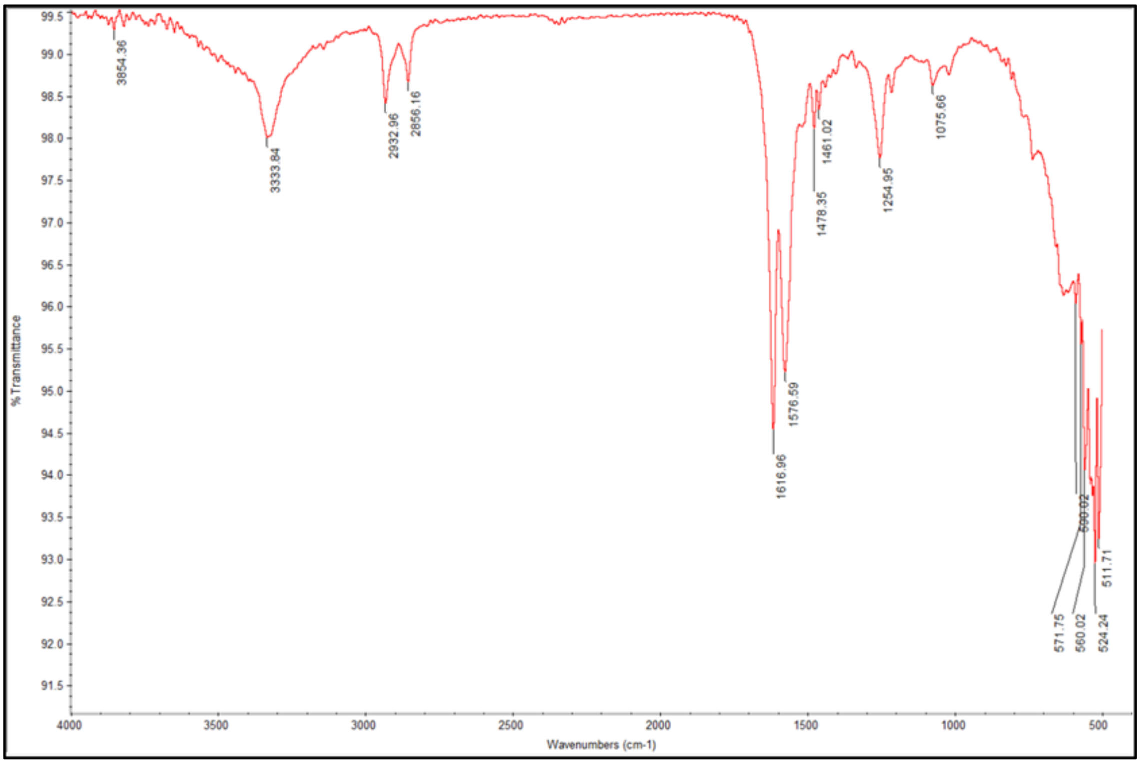


Figure 3.4 (b)

FT-IR spectra of CMC-PPUF

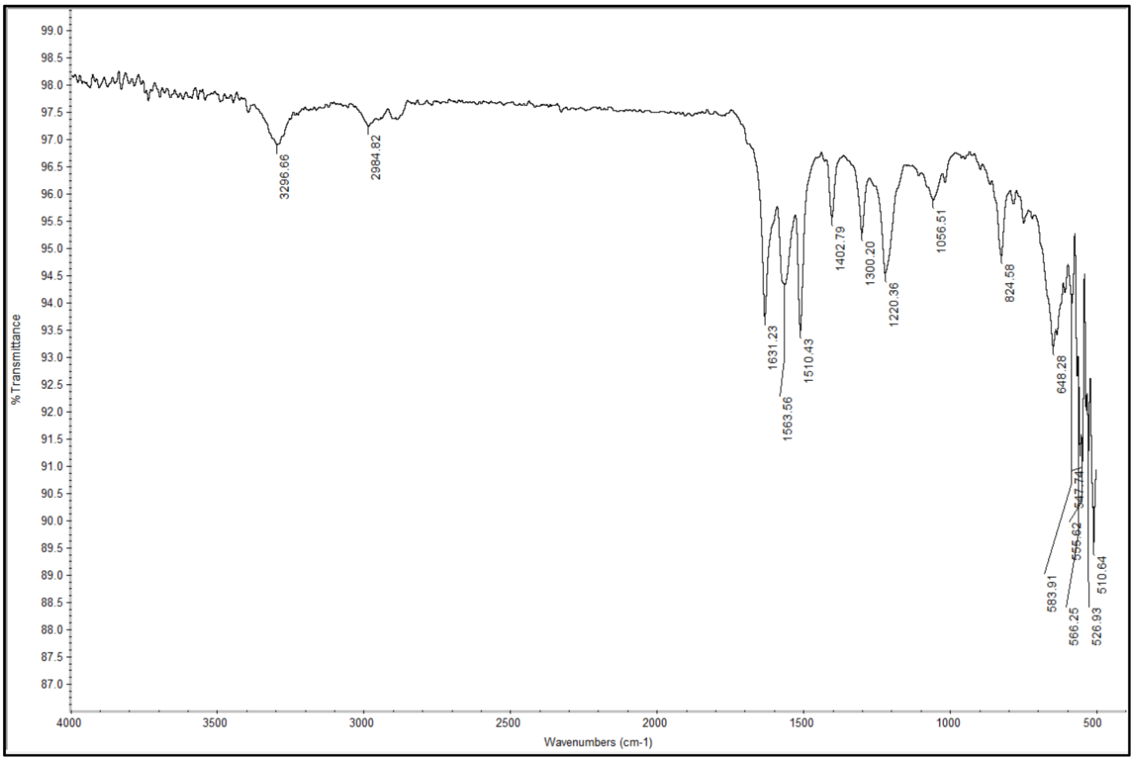


Figure 3.9

Model for the liquid film diffusion of Pb (II) adsorption onto HMPUF and PPUF

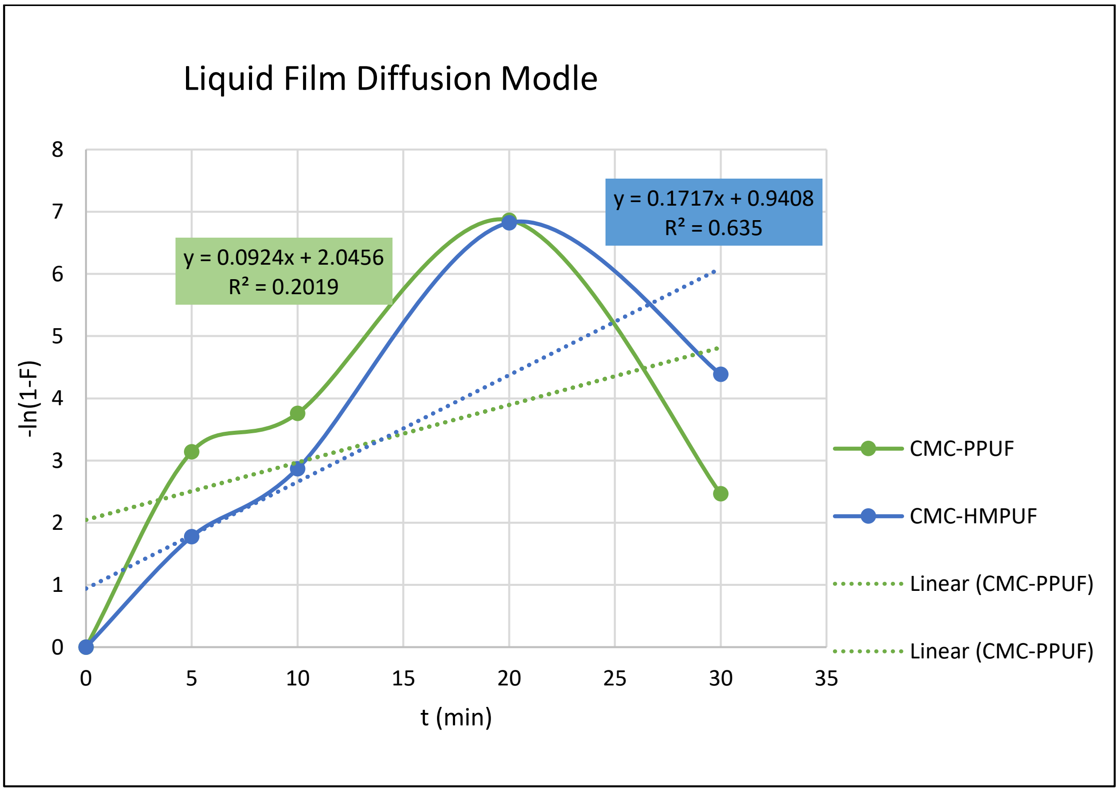
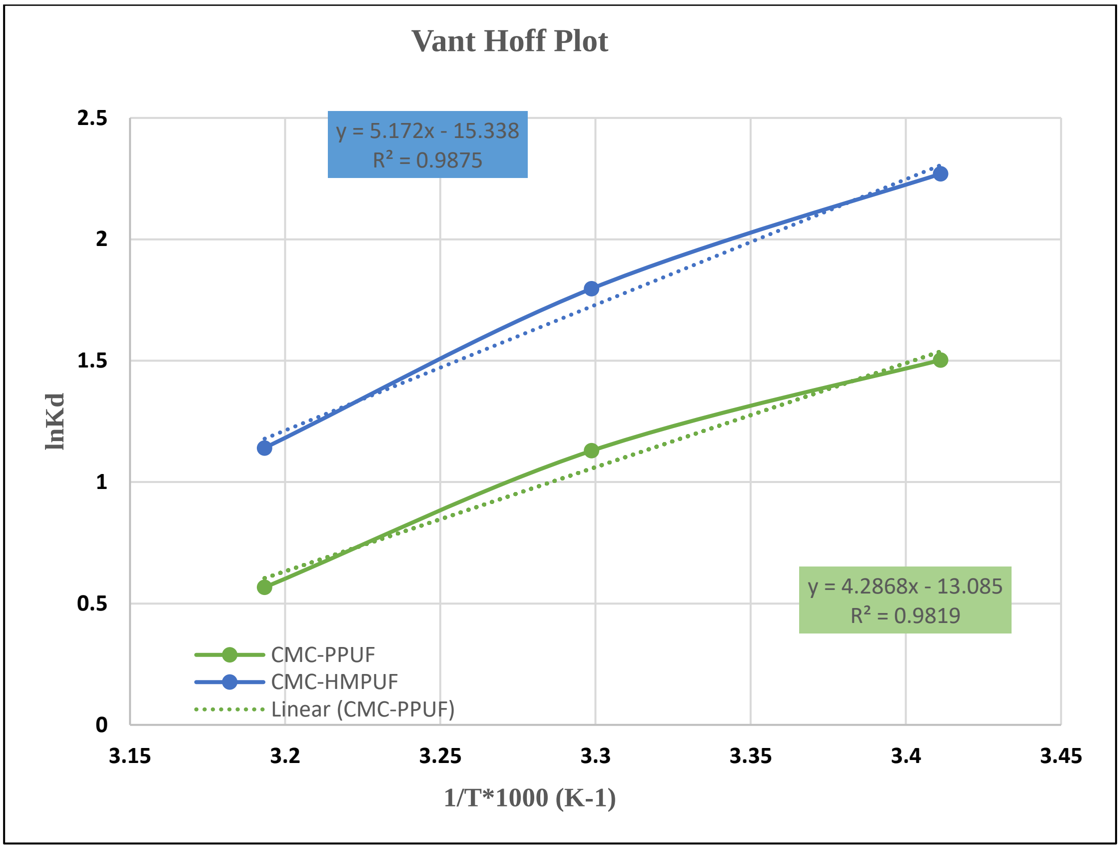


Figure 3.10

Van't Hoff diagram showing Pb^{2+} adsorption on CMC-HMPUF, CMC-PPUF.



Appendix B

Tables

Table 3.2

ICP-MS analysis results for efficiency of CMC-HMPUF and CMC-PPUF Polymers toward metal ions present in wastewater

Metal ions	Initial Conc. (ppm)	Final Concentration (ppm)		Removal (%)	
		HMPUF	PPUF	HMPUF	PPUF
Ag	0.192	0.021	0.014	89.06	92.71
Al	333.938	16.963	7.982	94.92	97.61
As	6.718	2.295	3.245	65.84	51.7
Ba	47.463	5.522	9.446	88.37	80.1
Be	0.061	0.012	0.017	80.33	72.13
Bi	9.109	1.18	0.79	87.05	89.35
Ca	113808.032	37151.77	49422.345	67.36	56.57
Cd	0.138	0.011	0.015	92.03	89.13
Co	0.66	0.129	0.105	80.45	84.09
Cr	13.139	3.197	5.718	75.67	65.48
Cu	24.245	2.216	1.425	90.86	94.12
Fe	903.125	103.281	40.969	88.56	95.46
Ga	0.734	0.301	0.4326	58.99	41.06
Li	18.341	2.277	1.729	87.59	90.23
Mg	78954.34	7243.602	8093.98	90.83	89.75
Mn	44.35	3.077	2.054	93.06	95.37
Mo	3.006	0.961	0.718	68.03	67.11
Ni	8.449	5.103	4.479	39.60	46.99
Pb	14.774	0.923	2.075	93.75	85.95
Se	31.949	13.148	14.983	58.85	53.1
Sr	514.581	281.3	352.551	45.33	31.49
Te	1.318	0.152	0.055	88.47	95.83
Tl	0.067	0.009	0.011	86.57	83.58
U	0.923	0.466	0.083	49.51	91.01
V	16.272	5.21	6.89	67.98	57.66
Zn	90.556	3.609	1.693	96.01	98.13

Table 3.4

Langmuir Adsorption values for CMC – HMPUF, CMC - PPUF

Langmuir isotherms					
Metal ion	Adsorbent	R^2	Q_{max}	K_L	R_L
Pb^{2+}	CMC - HMPUF	0.91	7.17	3.58	0.03
	CMC - PPUF	0.98	61.73	0.07	0.58

Table 3.6

Freundlich Adsorption Isotherms parameters for CMC-HMPPUF, CMC-PPUF

Freundlich isotherms				
Metal ion	Adsorbent	R^2	n	K_f
Pb^{2+}	CMC-HMPUF	0.99	1.15	4.21
	CMC-PPUF	0.99	1.57	2.98

Table 3.9

Intraparticle diffusion model values

Adsorbent CMC-	**Time (min)**	**$[Pb^{2+}]$ (ppm) C_e**	**q_t (mg/g)**	**$t^{1/2}$**
HMPUF	5	2.13	3.93	2.24
	10	1.07	4.46	3.16
	20	0.54	4.72	4.47
	30	0.65	4.67	5.48
	35	0.72	4.64	5.92
	45	0.92	4.54	6.71
PPUF	5	1.74	5.50	2.24
	10	1.57	5.62	3.16
	20	1.38	5.75	4.47
	30	2.10	5.27	5.48
	35	2.33	5.11	5.92
	45	2.47	5.02	6.71

Table 3.10

Kinetic adsorption parameters for the adsorption of Pb^{2+} on polymers CMC-HMPUF& CMC-PPUF

(a) Pb^{2+} adsorption kinetic parameters on CMC-HMPUF (pseudo-first- order model)

Metal ion	Adsorbent	R^2	Theo. q_e	Exp. q_e	K_1
Pb^{2+}	CMC-HMPUF	0.89	0.05	4.73	0.14
	CMC-PPUF	0.82	0.15	5.75	0.04

(b) Adsorption kinetic parameters for the adsorption of Pb^{2+} on CMC-HMPPUF/CMC-PPUF (pseudo-second order model)

Pb^{2+}	CMC-HMPUF	0.99	4.65	4.73	0.66
	CMC-PPUF	0.99	4.94	5.75	-0.15

(c)Kinetic adsorption parameters (Intraparticle diffusion model) for the adsorption of Pb^{2+} on polymers CMC-HMPUF& CMC-PPUF

Metal ion	Adsorbent	R^2	Z	K_{id}
Pb^{2+}	CMC-HMPUF	0.51	3.93	0.12
	CMC-PPUF	0.58	5.99	0.13

(d) Liquid film diffusion model values

Adsorbent CMC-	Time (min)	$[Pb^{2+}]$(ppm) C_e	q_t(mg/g)	Ln(1- F)
HMPUF $q_e = 4.73$	5	2.13	3.93	1.78
	10	1.07	4.46	2.87
	20	0.54	4.72	6.82
	30	0.65	4.67	4.39
	35	0.72	4.64	3.93
	45	0.92	4.54	3.21
PUF $q_e = 5.75$	5	1.74	5.50	3.14
	10	1.57	5.62	3.76
	20	1.38	5.75	6.86
	30	2.10	5.27	2.47
	35	2.33	5.11	2.19
	45	2.47	5.02	2.06

Table 3.11

Adsorption kinetic parameters (Liquid film diffusion model) for the adsorption of Pb (II) dsorption onto HMPUF and PPUF

Metal ion	**Adsorbent**	**R^2**	**K_{df}**
Pb^{2+}	CMC-HMPUF	0.64	0.94
	CMC-PPUF	0.20	2.05

Table 3.12

Thermodynamic value for Van't Hoff plots

Adsorbent CMC-	**Temperature (℃)**	**$[Pb]^{2+}$ (ppm) C_e**	**1/T 1000 (K^{-1})**	**lnK_d**
HMPUF	15	0.99	3.47	1.56
	20	0.52	3.41	2.21
	30	0.79	3.35	1.80
	40	1.51	3.25	1.14
PPUF	15	2.25	3.47	0.94
	20	1.28	3.41	1.50
	30	1.86	3.35	1.13
	40	3.27	3.25	0.57

جامعة النجاح الوطنية
كلية الدراسات العليا

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

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الملخص

الخلفية: الماء إكسير الحياة. إن الاستخدام المفرط للمواد الكيميائية في مختلف القطاعات سواء قي الصناعة، أو الزراعة او غيرها يمكن أن يؤدي الى زيادة حمل الملوثات في المياه. النويدات المشعة، المواد الكيميائية المنزلية، المستحضرات الصيدلانية، منتجات العناية الشخصية، الكائنات الحية الدقيقة ومواد السباكة الكيميائية غير العضوية وغيرها من الملوثات شائعة في المياه. تعد المعادن الثقيلة من أكثر هذه الملوثات ضررا بسبب آثارها الدائمة وسميتها حتى في التراكيز المنخفضة. ونتيجة لذلك أصبحت ازالة أيونات المعادن الثقيلة الخطرة من الماء أمرا بالغ الأهمية.

الهدف: الغرض من هذه الاطروحة هو إنشاء مادة ماصة جديدة تعتمد على رغوة البولي يوريثان PUF والتي تم تعزيزها بمجموعة وظيفية أيونية قادرة على إمتصاص المعادن الضارة من الماء بكفاءة.

المنهجية: تضمنت عملية تصنيع البوليمرات المستهدفة سلسلة من التفاعلات الكيميائية بين كربوكسي ميثيل سيليلوز CMC ومركبات ثنائي ايزوسينات (هكساميثيلين ثنائي ايزوسينات وفينيلين ايزوسينات) في وجود ثنائي أيزوبروبيل أمين كعامل محفز مما ادى الى تكوين المواد البوليمرية رغوة كربوكسي ميثيل سيليلوز–سداسي ميثيلين بولي يوريثان (CMC-HMPUF) ورغوة كربوكسي ميثيل سيليلوز–فينيلين ثنائي ايزوسينات البولي يوريثان (CMC-PPUF) مع روابط يوريتان.

النتائج: تم تقييم قدرة الامتزاز للرغاوي البوليمرية نحو الرصاص باستخدام مجموعة متنوعة من العوامل مثل درجة الحرارة، درجة الحموضة، جرعة الممتزات، الوقت، وتركيز الايون الاولي. بالإضافة الى ذلك تم اكتشاف القيمه المثلى لكل من المعلمات التي أدت للازالة الكمية للرصاص. كانت النسبة المئوية لازالة الرصاص بواسطة بوليمر CMC-HMPUF حوالي 95%، بينما كانت ل CMC-PPUF حوالي 87%.

تم ايضا دراسة الديناميكا الحرارية للامتزاز ،وعلم الحركة ومتساوي الامتزاز للحصول على نظرة ثاقبة لآلية وعفوية الامتزاز. أظهرت النتائج ان عملية امتزاز الرصاص (II) تصنف بأنها عملية طاردة للحرارة ($\Delta H^\circ < 0$) ، وتلقائية عند درجات حرارة منخفضة ($\Delta G^\circ < 0$)، ($\Delta S^\circ < 0$).

أظهرت المعلمات الديناميكية الحرارية والحركية التي تم الحصول عليها أن الامتزاز بواسطة الرغوتين يتوافق مع نموذج فروندليتش، ويتبع نموذج حركية الامتزاز من الدرجة الثانية.

أظهرت الرغاوي الناتجة ميلًا كبيرا لإزالة أيونات المعادن المتعددة الموجودة في عينة فعلية من مياه الصرف الصحي.

الخلاصة: تم تصنيع البوليمرات المستهدفة، وتم الكشف عن روابط اليوريتان باستخدام التحليل الطيفي للأشعة تحت الحمراء، وأظهرت رغوة البوليمرين ثباتا قويا، وكانت فعالة في ازالة المعادن الثقيلة من مياه الصرف الصحي.

الكلمات المفتاحية: البولي يوريثين، كربوكسي ميثيل سيليلوز، المعادن الثقيلة، هيكساميثلين ثنائي ايزوسينات، فينيلين ثنائي ايزوسينات.