An-Najah National University

Faculty of Graduate Studies

CROSSLINKED CELLULOSE WITH TRIDENTATE COORDINATION SITES: SYNTHESIS AND APPLICATION IN EXTACTION OF TOXIC METAL IONS FROM WASTEWATER

By

Shahd Hani Mahmood Shaheen

Supervisors

Dr. Ibrahim Abu Shqair

Prof. Othman Hamed

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

2023

CROSSLINKED CELLULOSE WITH TRIDENTATE COORDINATION SITES: SYNTHESIS AND APPLICATION IN EXTACTION OF TOXIC METAL IONS FROM WASTEWATER

By

Shahd Hani Mahmood Shaheen

This Thesis was Defended Successfully on 7/9/2023 and approved by

Dr. Ibrahim Abu Shqair Supervisor	Signature
Prof. Othman Hamed Co-Supervisor	Signature
Dr. Nizam Diab External Examiner	Signature
Dr. Shehdeh Jodeh Internal Examiner	Signature

Dedication

To myself, for my patience and persistence for success in spite of all challenges.

To my parents and the words of encouragement from my mom since childhood until now "I am proud of you, you can do it, you will have a bright future".

To my brothers and sisters, the sweetest and most kind family I have ever known.

To my little daughters "Nada" and "Leen" who taught me how to be strong to face all difficulties.

To my dear husband "Raafat", thanks for being by my side every step of the way. Thanks for helping me get up after every stumble.

To my occupied country Palestine and the capital "Jerusalem": our education is the way for victory and independence.

Acknowledgment

Praise be to God above all, who says in his book "Are those equal, those who know and those who do not know? It is those who are endued with understanding that receive admonition".

Special thanks to my supervisors, Dr. Ibrahim Abu Shqair and Prof. Othman Hamed for giving me the opportunity to work with them and benefit from their broad Knowledge and experience, thanks to their continuous follow up and advices that help me reach this stage.

Additionally, I would like to thank every teacher who taught me early in school and later on at the University (Arab American University and An-Najah National University).

Finally, big thanks to everyone who contributed to this achievement from near or far, I dedicate this work to you.

Declaration

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

CROSSLINKED CELLULOSE WITH TRIDENTATE COORDINATION SITES: SYNTHESIS AND APPLICATION IN EXTACTION OF TOXIC METAL IONS FROM WASTEWATER

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

Student's Name: Shahd Hani Shaheen

Signature: شهد شاهين

Date: 7/9/2023

List of Contents

Dedication III

Acknowledgment IV

Declaration V

List of Contents VI

List of Tables IX

List of Figures X

List of Schemes XI

List of Appendices XII

Abstract XIII

Chapter One: Introduction 1

1.1 General Review 1

1.2 Waste water treatment 4

1.3 Heavy metals 5

1.3.1 Copper 7

1.4 Adsorption 8

1.4.1 Characteristics of good adsorbents 9

1.5 Cellulose 10

1.5.1 Cellulose modification 13

1.5.2 Carboxyl methyl cellulose 14

1.6 Amino pyridine 16

1.7 Diethylene Triamine DETA 17

1.8 Scope of the study 18

Chapter Two: Experimental Part 19

2.1 Materials 19

2.2 Instrumentation 19

2.3 Polymer Synthesis..... 19
2.3.1 Preparation of carboxymethyl cellulose polymer functionalized with 2-aminopyridine (CMC-A) 19
2.3.2 Crosslinking of the CMC-A Polymer 20
2.4 Batch Adsorption Studies 20
2.4.1 Standard solution of copper (II)..... 20
2.4.2 Calibration curve for copper 20
2.4.3 Adsorption of Cu(II) by batch process..... 21
2.4.4 The effect of Cu^{2+} concentration on adsorption percentage 21
2.4.5 The effect of contact time on the adsorption of Cu^{2+} by CMC-A polymer 22
2.4.6 The effect of polymer dosage on adsorption efficiency 22
2.4.7 The impact of temperature on adsorption percentage of Cu2+ by CMC-A polymer 23
2.4.8 The effect of pH on adsorption efficiency of Cu^{2+} 23
2.5 Adsorption Isotherm 24
2.6 Adsorption Kinetics 25
2.7 Adsorption Thermodynamics 25
2.8 Waste Water Purification (Real Sample)..... 27
Chapter Three: Results And Discussion 28
3.1 Polymer Synthesis..... 28
3.1.1 Conversion of cellulose to carboxymethyl cellulose polymer..... 28
3.1.2 Conversion of carboxylic acid on the CMC to an ammonium carboxylate..... 29
3.1.3 Dehydration of the ammonium carboxylate to produce an amide..... 29
3.1.4 Polymer crosslinking by diethylene triamine 30
3.1.4.1 FT-IR analysis of the polymer 33
3.1.4.2 Thermal gravimetric analysis (TGA) of the polymer 33
3.1.4.3 Atomic Force Microscopy (AFM) for CMC-A polymer..... 34

3.2 Adsorption Results 35
3.2.1 Adsorption of Copper (Cu^{2+}) Ions 35
3.2.1.1 Effect of Cu^{2+} Initial Concentration 35
3.2.1.2 Effect of polymer dose 37
3.2.1.3 Influence of pH on adsorption 39
3.2.1.5 Effect of contact time 42
3.4 Adsorption Isotherms 43
3.4.1 Langmuir adsorption model 44
3.4.2 Freundlich isotherm model 44
3.5 Adsorption Kinetics 47
3.5.1 Pseudo-first order model 48
3.5.2 Pseudo-second order 48
3.6 Thermodynamics of Adsorption by CMC-A Polymer 49
3.7 Adsorption on a Real Samples of Sewage 51
3.8 Conclusion 51
3.9 Recommendations 52
List of Abbreviations 53
References 55
الملخص ..... ب

List of Tables

Table 2.1: Effect of adsorbate concentrations on the adsorption of Cu^{2+} ions. 22

Table 2.2: Effect of the contact time on the adsorption of Cu^{2+} ions..... 22

Table 2.3: Effect of the polymer dosage on the adsorption of Cu^{2+} ions. 23

Table 2.4: Effect of temperature on the adsorption of Cu^{2+} ions..... 23

Table 2.5: Effect of pH on the adsorption of Cu^{2+} ions. 24

Table 3.1: The Optimum Adsorption Parameters for adsorption of copper ions using CMC-A polymer…….. 43

Table 3.2: Langmuir and Freundlich model values for Cu^{2+} adsorption by CMC-A polymer…….. 45

Table 3.3: Langmuir and Freundlich isotherms parameters for CMC-A polymer 47

Table 3.4: Values of the pseudo-first order and pseudo-second order kinetic models... 48

Table 3.5: Kinetic parameters for the adsorption of cu^{2+} on CMC-A..... 49

List of Figures

Figure 2.1: The Calibration curve for Cu^{2+} 20

Figure 3.1: IR spectra of the Polymer 33

Figure 3.2: TGA for the CMC-A polymer 34

Figure 3.3: AFM image of the CMC-A polymer 35

Figure 3.4: The effect of initial ion concentration on the adsorption of Cu2+ ions 36

Figure 3.5: The effect of polymer dose on the adsorption of Cu^{2+} ions 38

Figure 3.6: The effect of pH value on the adsorption of Cu^{2+} ions 39

Figure 3.7: The effect of Temperature on the adsorption of Cu^{2+} ions 41

Figure 3.8: The effect of contact time on the adsorption of Cu^{2+} ions 42

Figure 3.9: Isotherm models for adsorption of cu^{2+} on CMC-A. 46

List of Schemes

Scheme 1.1: Molecular structure of (a) glucose (b) cellobiose and (c) cellulose polymer 11

Scheme 1.2: Intra and intermolecular hydrogen bonding in cellulose macromolecule .. 12

Scheme 1.3: Synthesis of CMC and the structural difference between cellulose and CMC polymers 15

Scheme 1.4: Chemical structure of(a) 2-amino-pyridine, (b) DETA 18

Scheme 3.1: Cellulose conversion to CMC polymer. 28

Scheme 3.2: Formation of an ammonium carboxylate from carboxylic acid of CMC .. 29

Scheme 3.3: Dehydration of ammonium carboxylate to produce amide 30

Scheme 3.4: CMC modification by 2-aminopyridine. 31

Scheme 3.5: CMC-A polymer crosslinking 32

List of Appendices

Appendix A: Tables 62

Table 3.6: The Thermodynamic values for Van't Hoff plots..... 62

Table 3.7: The thermodynamic parameters of Cu^{2+} adsorption on CMC-A polymer.62

Table 3.8: The ICP-MS analysis results for toxic metal concentrations adsorbed by CMC-A polymer..... 62

Appendix B: Figures 64

Figure 3.10: (a) The pseudo-first order Model for cu^{2+} adsorption on CMC-A polymer. (b) pseudo-second order model. 64

Figure 3.11: The Van't Hoff plot for Cu^{2+} adsorption on CMC-A..... 65

CROSSLINKED CELLULOSE WITH TRIDENTATE COORDINATION SITES: SYNTHESIS AND APPLICATION IN EXTRACTION OF TOXIC METAL IONS FROM WASTEWATER

By
Shahd Hani Shaheen
Supervisors
Dr. Ibrahim Abu Shqair
Prof. Othman Hamed

Abstract

Background: Water pollution that comes from industrialization and rapid urbanization has been considered as serious problem because water is one of the vital resources for life, and it is important to all humans, environment, society and economy. Heavy metals (Ag, Hg, Pb, Cr, Cu…) are among the contaminants that are of primary concern and need to be removed from waste water by various technologies that include adsorption as the wide used treatment process. Low cost and effective adsorbents from natural polymers are of great interest for heavy metal removal from waste water and researches have been directed toward modifying these natural adsorbents to enhance their adsorption efficiency.

Objectives: The main goal from this work is to prepare a crosslinked carboxymethyl-cellulose polymer functionalized with 2-aminopyridine in order to make it excellent binder to heavy metal for application in waste water purification.

Methodology: The method of preparing the polymer begins with a reaction between carboxymethyl cellulose (CMC) polymer and 2-aminopyridine to convert the carboxylic group into amide then crosslinking the prepared polymer by diethylene triamine (DETA) for extra stability. The resulting polymer was analyzed by Fourier Transform -Infra Red (FT-IR), Atomic Force Microscopy (AFM) and Thermal Gravimetric Analysis (TGA).

Results: The percent removal of Cu^{2+} ion by the prepared polymer was investigated under the following parameters: temperature, time, pH, adsorbent concentration and adsorbent dosage. The maximum removal of Cu^{2+} by CMC/2-aminopyridine polymer is 92.25% at pH = 7.23, temperature 19 ºC, time 20 min, adsorbent concentration 20 ppm and polymer

dose 10 mg. The adsorption isotherm, kinetics and thermodynamics were investigated to determine the mechanism and spontaneity of the adsorption process and the results revealed that it is exothermic ($\Delta H° < 0$), spontaneous ($\Delta G° < 0$) and occurs spontaneously at low temperatures ($\Delta S° < 0$). The adsorption follows Pseudo-second order model with ($R^2 = 0.99$) and the Langmuir adsorption isotherm was applied with ($R^2 = 0.93$)

Conclusion: The target polymer was prepared and confirmed by IR, it is thermally stable based on TG analysis and it results in high percent removal of the heavy metal.

Keywords: Carboxymethylcellulose, Water pollution, wastewater treatment, heavy metals, Copper, 2-aminopyridine, DETA

Chapter One
Introduction

1.1 General Review

One of the most important requirements of life in general for humans, animals, environment, agriculture, and economy is water, and the global need for fresh water is increasing due to the growth of human population and economy. The presence of water is the most necessary factor for construction of a civilization or to classify a particular place as eligible for housing.

The most essential human activities are relying on water such as respiration, nutrition, circulation, reproduction and excretion, and it is the main ingredient of the human body. Water acts as a biological solvent in the body, regulates the body temperature and has many, many other vital roles.

Water availability has been reduced due to several related reasons, some of that reasons are: increased population growth, rainfall, vegetation type, water runoff, temperature, global warming, climate change, evaporation rate and water pollution [1].

The fact that eight liters of fresh water are being affected and polluted by just one liter of waste water is a serious matter that requires action. Moreover, water pollution transmits from water to soil, then to plants through irrigation or to animals that drink from that polluted water [1].

The quality of drinking water is one of the most important factors that affect human health. But unfortunately, only 0.3% of water sources on earth could be considered usable. Moreover, these limited sources are facing many problems from shortening to pollution or unconscious use. The amount of sewage water being discharged every day to the freshwater is estimated about two million tons [1, 2].

Although it is a human right for everybody to have an access for safe water, many diseases are resulting from bad water quality or polluted water especially in developing countries, however, a good understanding of the effects of poor water quality on health can contribute to take the right actions in order to enhance the water conditions in various countries [2].

Water pollution is a problem that need to be overcome all around the world in order to reduce its bad effects on human health and environment [3]. About 80% of diseases (viral, parasitic and bacterial diseases) are transmitted by polluted water as reported by (WHO), and 3.1% of deaths is because of bad unhygienic water. These numbers and the fact that water for drinking in many countries is not compatible with the standards of WHO make the water pollution a worldwide affair and the situation requires more awareness and education to prevent or at least reduce water pollution [4].

Polluted water is responsible of many problems and diseases such as cholera, immune suppression, typhoid fever, respiratory diseases, neurological disorders, reproductive failure, acute poisoning, cardiovascular diseases, skin and kidney problems, diarrhea, gastroenteritis, vomiting and other diseases [4].

Water pollution happens when the proportions of natural water ingredients rise above their permissible and natural limit, and this is usually occurred as a result of unwanted material that enter the water and change its quality. Water pollution has harmful effects on living organisms and plants in the water bodies also on humans, plants and animals that might be subjected to polluted water [5].

Contaminants that causing the major water pollution is mostly resulted from various human made activities, industrial and domestic wastes, radioactive wastes, marine landfill. There are many types of pollutants which include acids, alkalis, fertilizers, detergents, household wastes, industry wastes, pharmaceutical, various metals especially heavy metals, organic toxic wastes and pesticides [1, 5].

The most harmful pollutant among all is heavy metals and toxins from industrial wastes. Industrial wastes that are discharged into rivers and water bodies without treatment are the main cause of water pollution for both surface water and ground water. As reported in literature, about 70% of water pollution is resulting from domestic sewage, around 25% is due to various industries, and the type of contaminants rely on the nature of industry [4, 5].

Heavy metals include copper, zinc, cadmium, mercury, lead, silver, arsenic, platinum, iron and chromium. Many of the heavy metals are toxic or even cause cancer. The main side effect of the heavy metals is that it is not biodegradable and accumulates inside the

body causing several organ damage and multiple diseases. Approximately 40% of the rivers and lakes have been subjected to pollution by heavy metals. Each heavy metal or polluting compound in general has a maximum allowed limit for its presence in water (the threshold limit), and this regulation is placed by WHO or other environmental regulation organizations [3].

Contaminated wastewater is released to the environment directly without treatment in nearly all countries except the highly developed ones, and this is for sure leads to bad effects on the ecosystem, the nearby freshwater, economy and human health [6].

Based on the above, the optimal solution for water pollution and water shortage is to provide a new water source and protect the existing ones by waste water recovery and reuse [1]. And waste water could be converted into better usable water by undergoing a waste water treatment technique. These techniques can be subdivided into primary, secondary and tertiary water treatment.

Organic material and solids are removed in the primary treatment, while secondary treatment deals with transformation of organic and inorganic pollutants into more safe materials. Finally, tertiary treatments comprise precipitation, crystallization, distillation, oxidation, photocatalysis, membrane technology and adsorption. In order to reach 99% removal efficiency of water pollutant, all steps become required and water should undergo the primary, secondary and tertiary treatment altogether [3].

Various waste water purification technologies have been implemented during the last decade aiming for the removal of contaminants and micropollutants, in an attempt to reduce the risk of wastewater reaching water bodies or drinking water. Four popular and widely applicable technologies are ozonation, activated carbon (AC), membranes and advanced oxidation processes, but none of them could be considered a universal technique for all contaminant, also each technique has some drawbacks which require research to be continue to overcome the current problems of the existing technologies and to find more efficient technologies [7].

Adsorption is one of the widely used and best methods Known for waste water treatment because it has the ability to adsorb various types of contaminants. Adsorption has a lot of

advantages such as: low energy consumption, high removal capacity and does not cause a secondary pollution [3].

Many types of materials have been studied to know the possibility of their use as adsorbents, since the adsorbent characteristics determine the efficiency of the adsorption process. The natural polymer cellulose and its derivatives have been under attention as adsorbent matrix because of cost effectiveness, high selectivity and high capacity [8].

1.2 Waste water treatment

In response to the decrease in water resources and continuous increasing water shortage, in addition to water pollution, research has been directed towards the possibility of using wastewater after purifying it from various pollutants and the reuse becomes a necessary condition.

Treated waste water could be used for irrigation of agriculture and landscape, also it could be used to recharge ground water. In addition, several applications could employ the treated water such as toilet flushing, washing purposes and fire protection. During the last years, scientists have developed several methods for waste water treatment to overcome the risks of thousands of micropollutants before reuse of that water.

Complete removal of micro-contaminants (chemical or biological) is a big challenge and much research have been directed toward developing technologies that have the ability to remove pollutants from waste water and boost safe reuse [7].

Traditionally, precipitation was used for heavy metals removal from water but the method is effective only at higher metal concentrations, in addition to a large quantity of sludge that is produced and need further treatment which considered not economical [9].

Later on, several methods have been used and the four famous and widely used ones include activated carbon, membranes, ozonation, and advanced oxidation processes (AOPs) Moreover, more than one single treatment process may be required depending on the final use of treated water because some types of microcontaminants are not completely removed from waste water by simple conventional techniques.

By comparing the four technologies previously mentioned, it was found that membrane filtration (both nano-filtration and reverse osmosis) presents higher prevention of

microcontaminants despite the fact that it generates lots of wastes. AOPs shows good ability for pollutant removal but still need more testing. Adsorption and Ozonation have comparable ability and efficiency in contaminant treatment [7].

The selection of the treatment technology to be used for heavy metal removal depends on several factors include: initial ions concentration, ingredients of waste water, cost and impact on environment.

Adsorption considered as the widely used technology for waste water treatment which is economic, effective and ends up with high quality treated water. Although activated carbon has been the most common used adsorbent, researchers now look for cheaper alternatives of natural origin to be used for heavy metals removal from waste water [9].

1.3 Heavy metals

Water pollution due to heavy metals is a worldwide environmental problem. Heavy metals are elements with density of more than 4 g/cm^3 and atomic weight higher than 40.04. These elements comprise Copper (Cu), silver (Ag), cadmium (Cd), zinc (Zn), mercury (Hg), lead (Pb), arsenic (As), platinum (Pt), chromium (Cr), and iron (Fe). These toxic metals are released everyday into water from different sources and its concentration in surface water exceed the maximum limit allowed for drinking water.

Nearly 40% of rivers and lakes have been contaminated by heavy metals. The problem with heavy metals is that it is not biodegradable so that it is accumulate and its concentration raise up in the living organisms [3]. It possesses excessive accumulation, biomagnification and toxicity. Heavy metals reach water from industry, sewage discharge, mining and fertilizers, soil erosion [10].

Very low concentrations of heavy metal ions are essential for many of biochemical and physiological activities in the human body, whereas large doses are classified as toxic or either carcinogenic. Exposure to heavy metals cause damage to brain, kidneys, lungs, prostate, liver, esophagus, skin and stomach, also neurodegenerative diseases, such as Parkinson diseases and Alzheimer. Moreover, heavy metals have a bad effect on the growth and survival of aquatic organisms and it causes death to unborn fetus. These effects make it necessary to find effective ways for heavy metals removal from water [3].

EPA limits of heavy metals in drinking water are 0.01 ppm for Arsenic, 0.0005 ppm for cadmium, 0.1 ppm for chromium, 0.015 ppm for lead, 0.002 ppm for mercury, 5 ppm for zinc and 1.3 ppm for copper. These numbers are a threshold limits or lines that separates the dose levels and it is the point limit at which the toxic effects can occur above that limit [11].

Cadmium from smelting or mining industry, sewage and fossil fuels burning are known to have toxic damage to kidneys, liver, lungs, placenta, bones and brain. And it causes a premature birth in the case of exposure during pregnancy.

Arsenic from industrial or agricultural activities is highly carcinogenic and it cause malignant growth in different body organs like liver, bladder, skin and lungs.

Zinc reaches water from various industries such as paints, batteries, cosmetics, pharmaceuticals and steal coatings; and it causes weakness of the immune system in the human body, weight loss and can impair important reactions at cellular level.

Industries like electroplating, textiles and leather tanning could expel Chromium to water within its effluents. Especially the hexavalent chromium has carcinogenic characteries for mammals in general and humans in particular [12].

Lead causes many harmful disorders in brain respiratory system and nervous system. Sources of lead are varied from electronic industry, petroleum and batteries.

Mercury the most toxic one released from pharmaceutical or agricultural industry leads to distortion in developing fetus, kidneys and brain. Also, lung damage, skin rashes, problems in hearing and vision and increased blood pressure [13].

Copper has toxic effects for humans and animals when present in high concentration [14, 15]. It is responsible for Wilson disease by causing damage at cellular level in humans [16].

1.3.1 Copper

Copper is a metal with a molecular weight of 63.546. It has a color close to red, it is found naturally in soil, sediment, rock, water and air, also exist in all animals and plants. Despite it could be an important metal for organisms at low concentration, its toxic effects appear at high levels.

Copper is an element from group 1B and it has different oxidation numbers, the most common are Cu (I) and Cu(II). Copper metal has many unique characteristics which vary according to the purity, such as: high electrical and thermal conductivity, low corrosion, pleasing appearance, alloying ability and malleability. In nature, many minerals contain copper like: chalcocite (Cu_2S), azurite ($2CuCO_3 \cdot Cu(OH)_2$), cuprite (Cu_2O), chalcopyrite ($CuFeS_2$), malachite ($CuCO_3 \cdot Cu(OH)_2$), and bornite ($Cu5FeS_4$). [17]

Cu(I) is unstable in water and tend to oxidized to Cu(II) or reduced to Cu metal. The only stable cuprous compound is the insoluble ones like CuF, Cu_2S and CuCN, so the exposure to copper will mainly be in the form Cu(II). Cu(II) form coordination complexes with organic and inorganic ligands.

Copper compounds are prepared industrially starting from copper metal, and the most important commercially produced copper compound is copper sulfate $CuSO_4$. Natural discharge of copper and its compounds to water and air could result from volcanic eruption and windblown dust. About 13% of copper released to water is in the form of copper sulfate. [17]

Copper element is used in water pipes, electrical wiring and alloys (bronze and brass). Also, it is used in agriculture to treat plant mildew. It is released to the environment by factories that use the copper metal in their industries (industrial effluents) or different ways like copper mining, fossil fuels, forest fires, natural soil weathering, domestic waste water, production of wood and production of phosphate fertilizers. In 2000 the estimated amount of copper released from industries into the environment was 640,000,000,000 grams. [17]

The levels of copper in the treated waste water from different industries was evaluated by EPA in 1981, and the results show that the mean level exceed 1 ppm whereas the maximum exceed 10 ppm. These industries along with the copper levels are as the

following: porcelain enameling (1.3, 8.8); gum and wood chemicals (1.4, 3.0) aluminum forming (<160, 2,200)); inorganic chemicals manufacturing (<1.6, 18); paint and ink formulation (<l.0, 60.0) and nonferrous metals manufacturing (1.4, 27.0). [17]

When high levels of copper enter the body from food, water or even breath, it spanned throughout the entire body by the blood stream causing anemia, immunotoxicity, kidney and liver damage and death in worst situation. Drinking copper contaminated water in particular causes vomiting, nausea, diarrhea and stomach cramps [17].

Copper accumulated in tissues leads to a genetic disorder named Wilson's disease. Exposure to high amounts of copper leads to bad effects to respiratory system, gastrointestinal, hepatic, endocrine, hematological and vision by the oxidative damage of macromolecules and membranes [18].

Environmental Protection Agency EPA is set a limit of less than 1.3 mg/L for Cu(II) in drinking water [19]. Because of that, the industrial waste water must be treated to lower the concentration of copper ion below that limit and prevent its harmful effects. To achieve this goal, various methods have been proposed for waste water treatment [20]. Also, drinkable water should undergo some treatment before reaching to homes in order to ensure matching with WHO recommendations [21].

1.4 Adsorption

The most favorable way for waste water treatment is Adsorption as reported by US EPA [22]. It is economic (inexpensive), safe (no harmful by products), effective, highly selective, possibility of heavy metal recovery and ends up with relatively low amount of sludge, because of that it is widely applicable way for heavy metal removal [23, 24, 25].

Adsorption process depends on the presence of the adsorbent molecule(solid) that attract the adsorbate to its surface by physical attractive forces or chemical binding, it could be described as the transfer of contaminant molecule onto the adsorbent surface.

While chemical adsorption (chemisorption) involves chemical bond formation by transfer or share electrons usually between metallic ions as the adsorbate and the adsorbent and it is endothermic, physical adsorption(physisorption) is happened duo to weak Van der Waals interactions, polarity and hydrogen bonding and it is exothermic [26, 27].

The adsorption efficiency or the amount of contaminant adsorbed on the adsorbent surface depends on several factors: the nature of both adsorbent and adsorbate, pH, temperature, contact time, concentration, foreign materials and surface structure and porosity of the adsorbent. Adsorption has been described as a green technology, since it results in high percentage of contaminant removal with no or very low toxic sludge [25].

Choosing suitable adsorbent is valuable factor for efficient adsorption process, and number of materials have been used and investigated as their ability to be a good adsorbent. Among these materials are: Activated carbon, chitosan, biochar, cellulose, vegetable waste, plants waste, bone ash, coal fly ash, coal, silica gel, resins, alumina, clay, zeolite, sawdust, brewery solid wastes, degreasing soybean, and metal nano-oxides. Researchers are still looking for alternative adsorbents with low cost and natural origin [25].

1.4.1 Characteristics of good adsorbents

A typical adsorbent should have unique characteristics such as large adsorption capacity and efficiency, large surface area, selectivity, low cost, safe to environment, fast adsorption, high mechanical strength, chemical stability, thermal stability, reusability, easy to separate from water and able to reduce pollutants to extreme low concentration.

Many of adsorbents were used intensively including metal oxides, activated carbon (AC), graphene oxides (GO), carbon nanotubes (CNTs), metal organic framework (MOF), nanoscale zero valent iron (nZVI), polymers, chitosan, clay minerals, biochar, waste-derived adsorbents and bio-adsorbents [28, 29].

High cost and difficulties in regeneration after adsorption of Activated carbon leads to shift the efforts toward finding cheaper alternatives [30]. In fact, scientific researches have been concentrated toward the production of adsorbents with higher capacity but also of low cost to solve the economic issue [27].

Low-cost adsorbent should be abundant material, needs little processing or being a waste material. Bio-adsorbents (agricultural and animal waste) and natural adsorbents (clay, zeolites, chitosan, pectin, chitin, cellulose, starch, lignin and red mud) have been preferred due to its low cost, biodegradability, recyclability, low accumulation and biocompatibility [31, 32].

Agricultural byproducts are considered a promising adsorbent because their use brings extra benefit more than just purifying waste water with a low-cost adsorbent, it is also lower the coasts needed for the disposable of that byproducts. Sugar beet pulp, castor tree leaf powder, coir pith, rice husk, coal fly ash and cellulose are natural adsorbents mentioned in the literature for adsorption of heavy metals from waste water [31].

1.5 Cellulose

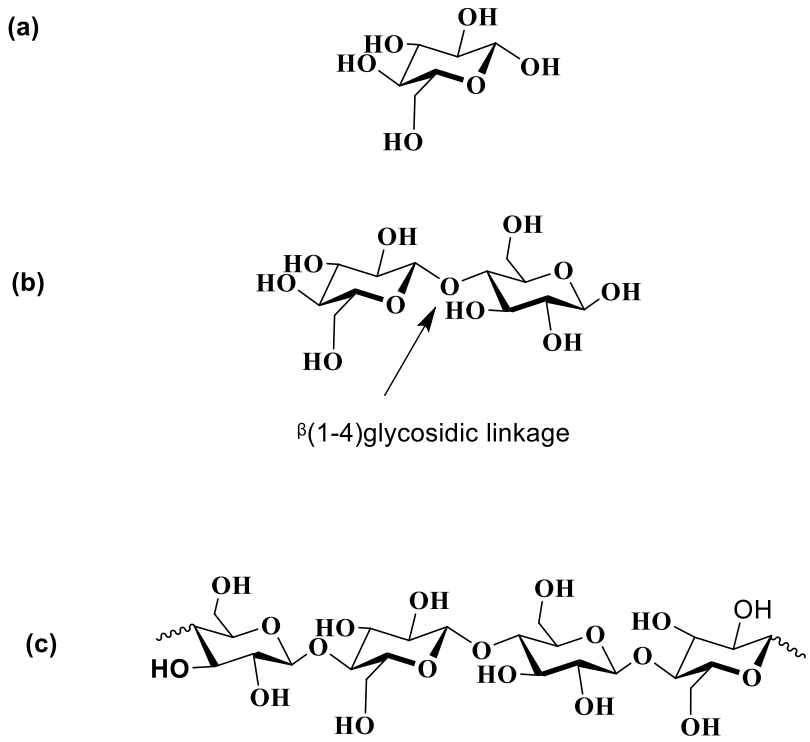
The natural polymer cellulose (the highly abundant biomass) and its derivatives has been reported as great materials for adsorption. The biopolymer cellulose has unique characteristics since it is abundant, low cost, biocompatible, biodegradable, non-toxic and easily modified [29, 32].

About 10^{11}-10^{12} tons of cellulose are produced every year, and this make it the most plentiful natural material. It has many advantageous characteristics such as it is biodegradable, non-toxic, cheap, tough, fibrous, water insoluble and easy to chemically modify it.

Sources of cellulose vary from cotton (98% cellulose), wood (90%) and other sources which differ in their cellulose content. The homopolymer cellulose with a chemical formula$(C_6H_{10}O_5)_n$ is consist from a repeating unit of D-anhydro glucopyranose (AGU) or typically known as glucose units as shown in scheme 1.1 [33].

Scheme 1.1

Molecular structure of (a) glucose (b) cellobiose and (c) cellulose polymer

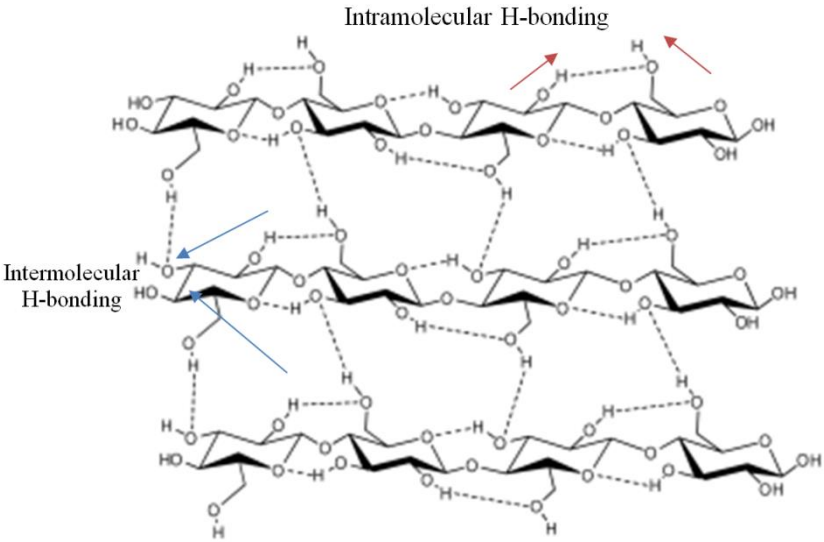


B-(l-4)-glycosidic bonds combine the glucose units together to form a cellobiose dimer. This glycosidic bond is a Covalent bond between C-4 OH group of one B-D-glucose and the carbon atom C-1 of the next glucose unit [33].

The number of repeated glucose units in the polymer molecule determines the length of the chain or the degree of polymerization (DP). DP of cellulose reaches 10,000 and more and this results in large molecular weight for the polymer [34].

Scheme 1.2

Intra and intermolecular hydrogen bonding in cellulose macromolecule



Note: this image was used to demonstrate the hydrogen bonding both inter- and intra-molecular in the cellulose polymer. "by Jasmani, L. and Thielemans, W. Preparation of Nanocellulose and its Potential Application. Forest Res. 2018; 7(3): 222"

Because of this hydrogen bonds shown in scheme 1.2 especially that happens between the cellulose molecules themselves cellulose aggregates as large precipitating molecule and it is insoluble neither in water nor in most other solvents [33, 35].

Natural cellulose contains both an amorphous and crystalline region. Crystalline structure forms from parallel cellulose chains and it is more dense than amorphous one. Acid hydrolysis of the native cellulose leads to break up the amorphous region and leave the crystalline one, which is the cellulose nano crystalline (CNC).

CNC have taken the researchers attention because it has all the advantages of cellulose and in addition higher strength and higher surface area. The characteristics of the CNC rely on the source of cellulose, type of hydrolysis acid, temperature and the time for the reaction [36].

1.5.1 Cellulose modification

For more than 150 years, cellulose based materials and derivatives have been used in various applications such as paper production, food, pharmaceuticals and waste water treatment [36].

In case of water treatment, modified cellulose has showed better capacity for contaminant removal than native cellulose because of improved chemical properties such as: Physical stability, sorption efficiency and chemical properties that is improved by modification of cellulose polymer. And that enhancement of cellulose characteristics by modification makes the modified cellulose more attractive to be used in various industries [33].

Variety of chemical modifications could be applied on cellulose polymer due to the presence of hydroxyl groups on the surface where a chemical reaction occurs preferably on C-6 (the primary hydroxyl). The number of hydroxyl groups being substituted refers to the derivatization extent or in other words the degree of substitution (DS) [37].

Carboxylation, carboxymethylation, oxidation, sulfonation, phosphorylation, cationization, silylation, esterification, polymer grafting, and many other reactions have been used to modify cellulose polymer and reported in literature [36].

Cellulose modified with pendent methyl benzalaniline chelating group has been synthesized and used as a new adsorbent for Cu^{2+} and Pb^{2+}. The results have shown that adsorption process is followed pseudo-second order model; also, it is spontaneous and exothermic one. The adsorption capacity of the modified cellulose was 157.3 mg/g for Cu^{2+} and 153.5 mg/g for Pb^{2+} [38].

Diethylenetriamine-bacterial cellulose was prepared and tested as adsorbent for Cu^{2+} and Pb^{2+}, the adsorption followed pseudo second order kinetics and the adsorption capacity were 63.09, 87.41 mg/g for copper and lead ions respectively [39].

Cellulose acetate/zeolite composite was synthesized and studied as adsorbent for the Cu^{2+} and Ni^{2+} metal ions, the adsorption process followed second order kinetics with maximum adsorption capacity of 28.57 and 16.95 mg/g for copper and nickel ions respectively. The adsorption process happens spontaneously in spite of it is endothermic one [40].

Cellulose modified with thio-semi carbazide had shown removal capacity106.3829 mg/g toward Cu^{2+} at pH = 6 and the reaction is spontaneous, exothermic and followed pseudo second order kinetics [41].

In another study, carboxymethylated cellulose nanofibrils was prepared and the result is high removal capacity 115.3 mg/g for Cu^{2+} at pH = 5.0 and the adsorption kinetics fits the pseudo-second order model [42].

Many other researches on cellulose modification by various functionalities has been reported in literature and studied for the ability to enhance the adsorption capacity of cellulose polymer.

1.5.2 Carboxyl methyl cellulose

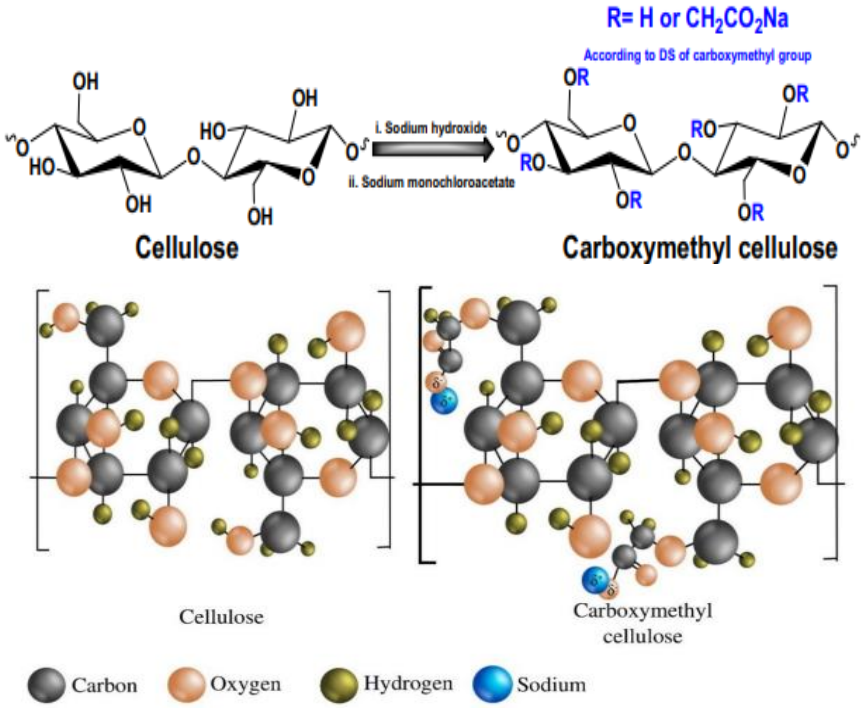
Carboxymethylcellulose (CMC) is, one of the cellulose derivatives with outstanding characteristics that make it a promising material in different applications and one of the most used derivatives of cellulose.

CMC is anionic, available, water soluble, its raw materials are abundant, it has low-cost synthesis, has a mechanical strength and tunable hydrophilicity. All these outstanding and unique properties make CMC polymer more preferable and more attractive than cellulose polymer [43].

When some carboxymethyl groups substitute the atom of hydrogen of some hydroxyl groups of cellulose, that leads to cellulose convert to CMC. The structure of the CMC polymer and the structural difference between cellulose and CMC polymers are shown in scheme 1.3. The first synthesis of CMC was in 1918 whereas commercial production began in 1920s [43].

Scheme 1.3

Synthesis of CMC and the structural difference between cellulose and CMC polymers



Note: this image was constructed to view the synthesis of CMC "by V. Kanikireddy et al. International Journal of Biological Macromolecules. 2020. 164. 963–975 "[73]and the structural difference "by Rahman, M. S. et al. Recent Developments of Carboxymethyl Cellulose. Polymers. 2021; 13: 1345".

The number of carboxymethyl group attached is the degree of substitution (DS), and for each anhydro-glucose unit the DS is range usually from zero to three. The DS value has a significant role in determining the CMC polymer unique characteristics like solubility, thickening property, viscosity, emulsibility, stability, acid resistance, and salt tolerance properties [43].

Because of that several advantages it is now has a wide application in many fields and large number of researches have been discussed different uses of CMC polymer in different applications, for example: paper, plastic, food, pharmaceutical, cosmetics and textile industries, also in biomedical engineering, drug delivery, energy production, storage energy production and wastewater treatment.

CMC-based polymers have been studied for their efficiency to remove various types of harmful pollutants from waste water, among these pollutants are dyes, radioactive species and inorganic anions and cations especially heavy metals [43].

In the past years, many researchers have been used hybrid materials of CMC crosslinked with different compounds in waste water treatment. For example, a nano adsorbent of CMC/Fe_3O_4 was synthesized in 2018 by Salama et al. and used to remove methylene blue dye from polluted water, the adsorption kinetic follow pseudo-second order and the adsorption capacity is 64 mg/g at pH = 7 [44].

In 2018 also CMC/Polyurethane composite was prepared by Hong and his workers and used for industrial water treatment from various harmful metals. The adsorption capacity was up to 216.1 mg of Pb^{2+}, 98 mg of $Cd^{2+}$and 78.7 mg of Cu^{2+} [43].

Chitosan/CMC adsorbent was synthesized using arginine cross linker and the adsorption capacity of Cd^{2+} and Pb^{2+} ions was up to 168.5 mg/g and 182.5 mg/g, respectively at pH = 6.5 and the adsorption process follows pseudo second order kinetics [45].

Fibrous CMC crosslinked with epichlorohydrin was demonstrated in 2015 by Wei et al. It is found that adsorption capacity of Cd^{2+} was up to 150.6 mg/g at pH = 6 [46].

In 2019, Gasemloo et al. designed sulfated-CMC-based nano-filter membrane that is cross-linked with glutaraldehyde. The synthesized polymer showed high adsorption efficiency toward Cr (VI) ions. The maximum percent removal of the Cr(VI) pollutant was 79.85% at pH = 4 [47].

In this work, we aim to prepare CMC polymer modified with 2-aminopyridine to form amide functionality and crosslinked with DETA, then study the ability for the prepared polymer to be used as adsorbent for heavy metals removal from waste water especially copper metal ions.

1.6 Amino pyridine

The reagent 2-aminopyridine has the chemical formula $C_5H_6N_2$ or $NH_2C_5H_4N$, its chemical structure is shown in Scheme 1.4(a). It appears as white powder or crystals or light brown solid. Its molecular weight is 94.11g/mol, and it is soluble in water and alcohol. It does melt at 58.1 ºC.

Aminopyridine is widely used in medical applications and pharmacology to manufacture dyes and drugs, and in analytical chemistry as a reagent or intermediate in chemical reactions [48, 49].

It is one of several chemicals that are added to certain polymer in order to enhance the adsorption capacity and percent removal by loading certain functional groups on the target polymer [50].

CMC functionalization with 2-aminopyridine will lead to enhance the removal efficiency and selectivity for heavy metal ions because aminopyridine is rich in nitrogen atoms and these nitrogen atoms have the ability to bind with heavy metals preferentially and strongly [51].

In previous researches, aminopyridine was used to functionalize different polymers to improve their adsorption capacity and contaminant removal efficiency, for example it was used with polystyrene polymer and the result was excellent adsorption for Pb, Cu and Hg ions [52].

Also, a cross-linked magnetic chitosan-2-aminopyridine glyoxal Schiff's base was prepared and used for adsorption of certain metal ions like Cu(II), Cd(II) and Ni(II) ions and it is found that the modification by aminopyridine leads to enhancement in the metal uptake of chitosan due to the availability of active groups to bind or chelate the metal ions, as mentioned in literature [50].

1.7 Diethylene Triamine DETA

One of diethylene triamine functions is a reinforce crosslinker that is used to crosslink the polymer strands together in order to increase its density and thermal stability [53].

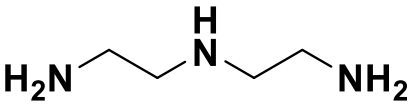
Its chemical structure is shown in Scheme 1.4(b).

Scheme 1.4

Chemical structure of(a) 2-amino-pyridine, (b) DETA

(a)

(b)



1.8 Scope of the study

The main goal of this work is to synthesize crosslinked modified carboxymethyl cellulose (CMC) polymer with tridentate receptor sites and investigate its ability to adsorb heavy metal ions (Cu^{2+}) from wastewater. The carboxymethylcellulose polymer modified by 2-aminopyridine is expected to have multi coordination sites necessary for binding heavy metal ions for purification of waste water.

Specific objectives are the following:

1. Synthesize the polymer by reacting CMC with 2-aminopyridine to form CMC/2-aminopyridine polymer with amide functionality.
2. Crosslinking the prepared polymer by using DETA crosslinker for increase polymer strength and thermal stability and number of binding sites.
3. Characterize the new polymer by various spectroscopic techniques (FT-IR, AFM, ICP-MS and TGA)
4. Evaluate the possibility of using the prepared polymer in water purification from toxic heavy metals.

Chapter Two
Experimental Part

2.1 Materials

All chemicals employed in this study were obtained from Sigma Aldrich Company.

The following are the chemicals that were used: 2-amino pyridine, diethylene triamine, carboxy methyl cellulose (CMC), methanol and copper sulfate ($CuSO_4.5H_2O$).

For solutions preparation, distilled water was used.

2.2 Instrumentation

The following instruments were used in this investigation: water shaking and heating bath (Daihan Labtech, 20.0 to 250.0 rpm Digital Speed Control), pH meter (JENWAY, model: 3510), Fourier-Transform Infrared Spectrophotometer (FT-IR) (Nicolet iS5, iD3 ATR, Thermo Fisher Scientific), Inductively Coupled Plasma Mass Spectrometer ICP-MS (ICE 3xxx C113500021 v1.30), Atomic Force Microscopy (AFM), Flame Atomic Absorption Spectrometer (ICE 3000 series AA System, Thermo Scientific) and Thermogravimetric analyzer (TGA).

2.3 Polymer Synthesis

2.3.1 Preparation of carboxymethyl cellulose polymer functionalized with 2-aminopyridine (CMC-A)

CMC (1.0 g, 0.006 mol/ anhydro-glucose repat unit) was dissolved in (90 ml) distilled water, when it is completely dissolved, a (0.5 g, 0.005 mol) of 2-aminopyridine was added. The reaction results in formation of an ammonium salt.

The reaction mixture was heated in the oven at (110 ºC) to evaporate the water; then the dry salt was subsequently heated by rising up the temperature to (160 ºC) for 30 minutes for complete dehydration and condensation to produce the amide functionality.

Finally, the solid was ground and washed with methanol before characterization.

2.3.2 Crosslinking of the CMC-A Polymer

Crosslinking was achieved by adding 0.2 ml of DETA to the reaction mixture before heating.

2.4 Batch Adsorption Studies

2.4.1 Standard solution of copper (II)

A stock solution of Cu (II) in distilled water with a 1000 ppm concertation was made by dissolving 3.93 g of $CuSO_4.5H_2O$ (249.5 g/mol) in a 1000 mL distilled water in a volumetric flask. A working solution (100 ppm) was prepared by diluting the stock solution in a 250 ml volumetric flask. The working solution was used to prepare standard solutions of Cu (II) with various concentrations ranging from 1.00 to 50.00 ppm.

The effect of the following parameters on the efficiency of adsorption were studied: time, dosage, temperature, initial concentrations, and pH.

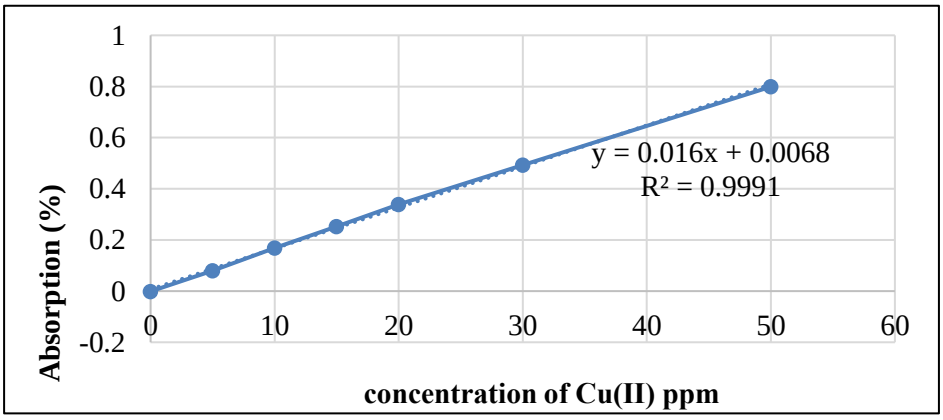
Flame atomic absorption spectroscopy (FAAS) was used to determine the final concentrations of heavy metal ion Cu (II).

2.4.2 Calibration curve for copper

Calibration curves for Cu^{2+} ions were constructed by measuring the absorbency of the standard copper solutions. (Figure 2.1)

Figure 2.1

The Calibration curve for Cu^{2+}



2.4.3 Adsorption of Cu(II) by batch process

This experiment was performed by adding a known quantity of the polymer to a known concentration of copper solution in a container, which was then placed in a water bath with a thermostat shaker. Then, all samples were filtered (using microfiltration) and analyzed for the residual Cu^{2+} concentration. FAAS was used to determine the concentration of Cu^{2+}.

Percentage of adsorption also known as the Removal percentage (E%) and equilibrium adsorption capacity (q_e) were calculated by using equations 1 and 2 shown below [54, 55].

$$q_e = \left(\frac{(C_0 - C_e)}{m}\right) \times V \qquad \text{Eq. 1}$$

$$E\% = \left(\frac{(C_0 - C_e)}{C_0}\right) \times 100\% \qquad \text{Eq. 2}$$

Where:

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

V: volume of Cu^{2+} solution (L).

m: mass of adsorbent (g).

C_0: initial concentration of Cu^{2+} (mg/L).

C_e: the equilibrium concentration of Cu^{2+}(mg/L).

2.4.4 The effect of Cu^{2+} concentration on adsorption percentage

To determine the Cu^{2+} metal ion concentration that contributes to maximum adsorption, five samples were prepared by mixing 10 mg of polymer with 10 ml of different Cu^{2+} ion concentration 5, 10, 20, 30, 50 ppm), while other conditions were kept constant (Temperature = 18 °C, time = 20 min, pH = 7.2).

FAAS was used to measure the remaining concentration of Cu^{2+} ions (final concentrations) and the results are shown in table 2.1

Table 2.1

Effect of adsorbate concentrations on the adsorption of Cu^{2+} ions

Initial concentration of Cu^{2+} (ppm)	Final concentration of Cu^{2+} (ppm)	Adsorption (%)	Residual (%)	Q_e (mg/g)
5.0	0.61	87.8	12.2	4.39
10.0	1.01	89.9	10.1	8.99
20.0	1.69	91.55	8.45	18.31
30.0	7.33	75.57	24.43	22.67
50.0	13.86	72.28	27.72	36.14

2.4.5 The effect of contact time on the adsorption of Cu^{2+} by CMC-A polymer

To study the impact of contact time on the adsorption process of Cu^{2+} by the prepared polymer CMC-A, five solutions were prepared by mixing 10 ml of the 20 ppm Cu^{2+} solution (the concentration that contributes to the highest adsorption) with 10 mg polymer at 18 °C, and pH = 7.2. The only variable is the time, and final concentration of copper ions were determined by the FAAS; the results are illustrated in **table 2.2**

Table 2.2

Effect of the contact time on the adsorption of Cu^{2+} ions

Contact time (min)	Initial concentration of Cu^{2+} (ppm)	Final concentration of Cu^{2+} (ppm)	Adsorption (%)	Residual (%)	Q_e (mg/g)
5	20.0	2.98	85.1	14.9	17.02
15	20.0	1.89	90.55	9.45	18.11
20	20.0	1.74	91.3	8.7	18.26
25	20.0	2.02	89.9	10.1	17.98
40	20.0	2.06	89.7	10.3	17.94

2.4.6 The effect of polymer dosage on adsorption efficiency

The effect of CMC-A polymer dosage on Cu^{2+} adsorption efficiency was studied by mixing four samples of 20 ppm Cu^{2+} ion concentration (the volume of each sample is 10 ml) with different CMC-A polymer dose (5,10,15,25 mg) at room temperature (18 °C) at pH = 7.2 and the four samples were Shaked in a thermostat water bath for 20 minutes. The results are shown in table 2.3 which presents the final concentration of Cu^{2+} ions that was analyzed by the FAAS.

Table 2.3

Effect of the polymer dosage on the adsorption of Cu^{2+} ions

Polymer dosage (mg)	Initial concentration of Cu^{2+} (ppm)	Final concentration of Cu^{2+} (ppm)	Adsorption (%)	Residual (%)	Q_e (mg/g)
5	20.0	2.12	89.4	10.6	35.76
10	20.0	1.55	92.25	7.75	18.45
15	20.0	3.04	84.80	15.2	11.31
25	20.0	3.25	83.75	16.25	6.70

2.4.7 The impact of temperature on adsorption percentage of Cu2+ by CMC-A polymer

The study of temperature effect on adsorption efficiency was done by mixing four solutions of Cu^{2+} ions, (20 ppm concentration, sample volume = 10 ml) with 10 mg polymer (the optimum dose that corresponds to the highest adsorption) at pH = 7.2. Each sample of the four was adjusted at certain temperature and Shaked for 20minutes.

FAAS was used to determine the final concentration of Cu^{2+} ion and the results are tabulated in Table 2.4

Table 2.4

Effect of temperature on the adsorption of Cu^{2+} ions

Temperature (℃)	Initial concentration of Cu^{2+} (ppm)	final concentration of Cu^{2+} (ppm)	Adsorption (%)	Residual (%)	Q_e (mg/g)
19	20	1.71	91.44	8.56	18.29
33	20	1.85	90.73	9.27	18.15
40	20	1.98	90.12	9.88	18.02
60	20	2.42	87.90	12.10	17.58

2.4.8 The effect of pH on adsorption efficiency of Cu^{2+}

The impact of varying the pH on the percentage of adsorption was evaluated by preparing five solutions (concentration 20 ppm Cu^{2+}, 10 ml sample volume) at pH range from 3-10, keeping the other conditions constant (temp = 18 ℃, time = 20 min, polymer dose = 10 mg).

The remaining concentration of Cu^{2+} was measured using FAAS and the results are illustrated in table 2.5 which represents the calculated percentage of adsorption, residual and equilibrium adsorption efficiency.

Table 2.5

Effect of pH on the adsorption of Cu^{2+} ions

pH	Initial concentration of Cu^{2+} (ppm)	Final concentration of Cu^{2+} (ppm)	Adsorption (%)	Residual (%)	Q_e (mg/g)
3.88	20.0	17.44	12.81	87.19	2.56
4.53	20.0	13.45	32.73	67.27	6.55
6.34	20.0	2.73	86.38	13.62	17.27
7.23	20.0	2.41	87.93	12.07	17.59
9.86	20.0	6.21	68.95	31.05	13.79

2.5 Adsorption Isotherm

At equilibrium, the relation between the quantity of the adsorbate being adsorbed per unit weight of adsorbent and the amount left in the solution represents the adsorption isotherm and that relation could be represented or studied by two different isotherm models.

Freundlich and Langmuir isotherm models are the most frequent models that used to describe mono-component and short-term adsorption of several metal ions [56]. These two models are used to examine the distribution of the adsorbate (metal ions) on the surface of adsorbent (solid polymer) at constant temperature.

Langmuir model which can be represented by (Equation.3), suppose that adsorbate forms a monolayer on a homogeneous surface of the polymer (adsorbent) [57].

$$\frac{1}{q_e} = \frac{1}{(Q_{max}\, K_L\, C_e)} + \frac{1}{Q_{max}} \qquad \text{Eq.3}$$

Where;

C_e: the equilibrium concentration of adsorbate(ppm)

Q_e: is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium(mg/g)

q_{max}: the theoretical maximum monolayer adsorption capacity of the adsorbent (mg/g)

K_L: Langmuir constant (L/mg)

Whereas the Freundlich model which is represented by (Equation.4) is applied when the adsorption happens between the adsorbate and the adsorbent with heterogeneous surface (non-uniform).

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \quad \text{Eq.4}$$

Where;

K_f is the Freundlich constant (mg/g).

2.6 Adsorption Kinetics

Adsorption kinetics gives important information about the mechanism of the adsorption process and its pathway. Kinetic models for the adsorption process are either pseudo–first-order (Equation.5) or pseudo– second-order. (Equation.6) [58]. The adsorption of heavy metals is best fitted with pseudo- second order model as concluded from previous researches.

$$\ln(q_e - q_t) = lnq_e - K_1 t \quad \text{Eq.5}$$

$$\frac{t}{q_t} = \frac{1}{(K_2 q^2)} + \left(\frac{t}{q_e}\right) \quad \text{Eq.6}$$

Where;

q_t: the mass adsorbate/adsorbent mass at time t (mg/g).

q_e: mass of adsorbate at equilibrium / mass of adsorbent (mg/g)

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

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

First order rate constant is determined from the plot of ln (qe − qt) against t, whereas the second order rate constant is determined from the plot of t/qt against t. R^2 value gives the indication of whether the adsorption follows pseudo first order kinetics or pseudo second order kinetics.

2.7 Adsorption Thermodynamics

Thermodynamic are used to predict or identify if the adsorption process is spontaneous or nonspontaneous, endothermic or exothermic by calculating different parameters such as: The activation energy (E_a.), Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°).

The thermodynamic parameters are calculated according to the following equations [58, 59, 60].

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

ΔG° : change in Gibbs free energy (J/mol).

ΔH °: change in enthalpy (J/mol).

T: absolute temperature (K).

ΔS°: change in entropy (KJ/mol. K).

Negative value of ΔG indicates a spontaneous reaction while a positive value indicates a nonspontaneous process. Negative ΔH means that the reaction is exothermic while positive value means endothermic process. It is worth mentioning that a negative value of ΔS means that adsorption results in order and the internal structure of the adsorbent does not subject to significant change through the process of adsorption, while positive ΔS reflects an increase in concentration of the adsorbate at the surface of adsorbent that means greater affinity of the adsorbent toward the adsorbate [53].

Eq.8 shows the relation between the equilibrium constant and gibs free energy $\Delta \boldsymbol{G}°$.

$$\Delta G° = -RTlnk_c \quad \text{Eq.8}$$

R: the universal gas constant (8.314 J.mol^{-1}. K^{-1}).

K_c: the thermodynamic equilibrium constant that equals ($\frac{q_e}{Ce}$) with a unit of (mol or L/g).

Substitution of equation 8 into equation 7 gives equation 9:

$$-RTlnk_c = \Delta H° - T\Delta S° \quad \text{Eq. 9}$$

Then if divided both sides by RT, this gives equation 10

$$lnk_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad \text{Eq.10}$$

From the plot of lnK versus (1/T), the value of ΔH° could be found from the slope which equals -ΔH°/R and the value of ΔS° could be calculated from the intercept which equals ΔS°/R.

2.8 Waste Water Purification (Real Sample)

To assess the prepared polymer ability to remove toxic metals from waste water, it was used for adsorption in a real sample from a Palestinian sewage water (An-Najah National University).

The experiment was done using 10 ml of the sewage water as a blank and other 10 ml mixed with the optimum dose of the polymer, (other conditions adjusted at the optimum values for the adsorption process).

The ICP-MS was used to identify the metal ions present in the sewage sample before and after adding the polymer, and this analysis was performed at An-Najah National University's Water Center in Nablus.

Chapter Three

Results And Discussion

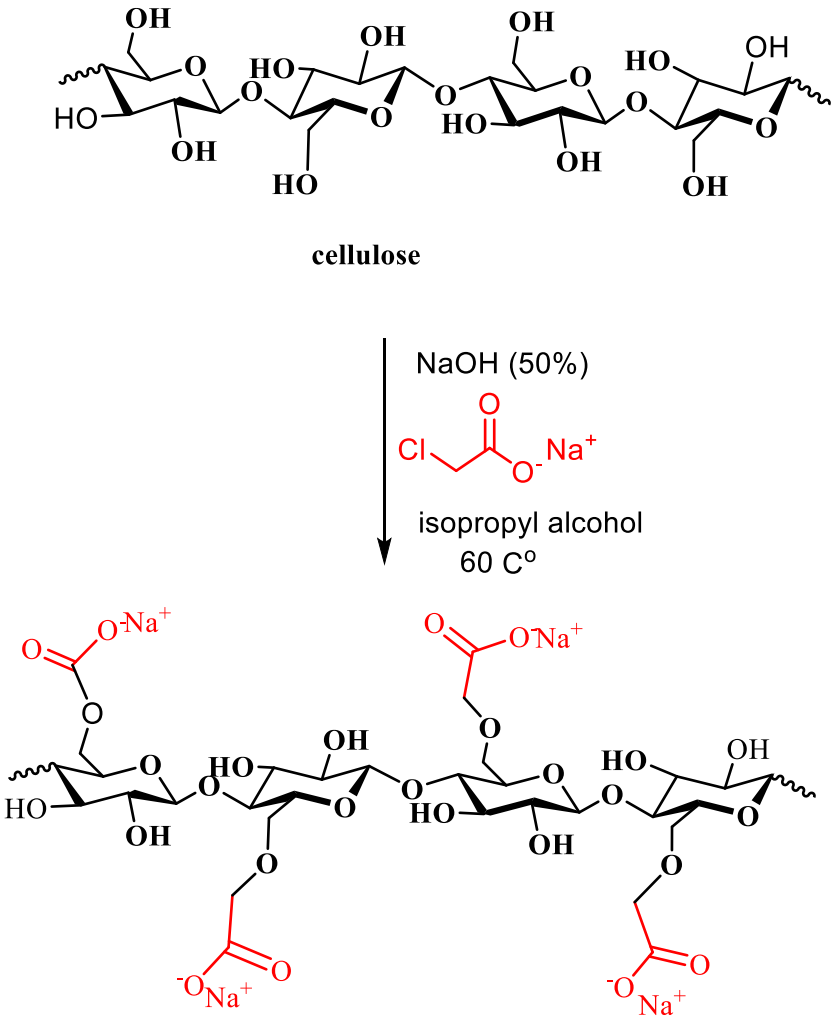
3.1 Polymer Synthesis

3.1.1 Conversion of cellulose to carboxymethyl cellulose polymer

The conversion of cellulose polymer to CMC are illustrated in **Scheme 3.1**. It was done by reacting cellulose with sodium chloroacetate in presence of NaOH. The reaction was carried out in isopropyl alcohol.

Scheme 3.1

Cellulose conversion to CMC polymer

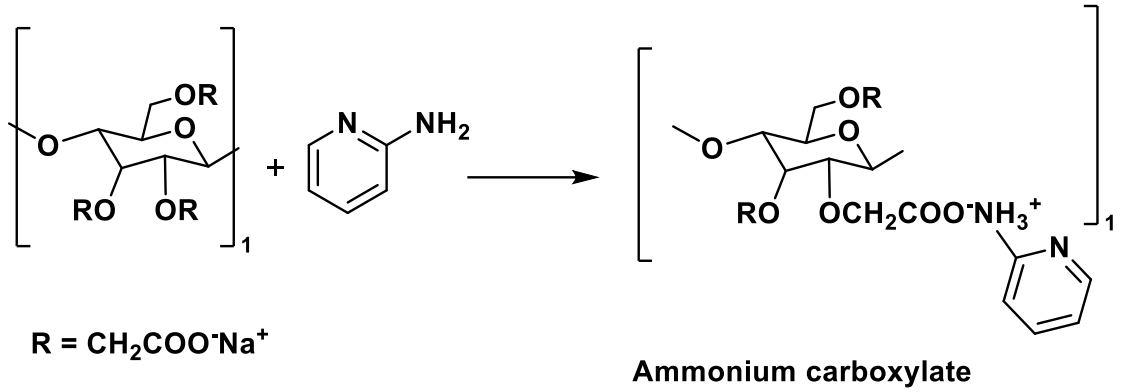


3.1.2 Conversion of carboxylic acid on the CMC to an ammonium carboxylate

The first step in the polymer synthesis is conversion of some carboxylic groups on CMC into ammonium carboxylate or ammonium salt by a rection between carboxymethyl cellulose and 2-aminopyridine which results in formation of an ammonium salt as shown in **Scheme 3.2**.

Scheme 3.2

Formation of an ammonium carboxylate from carboxylic acid of CMC



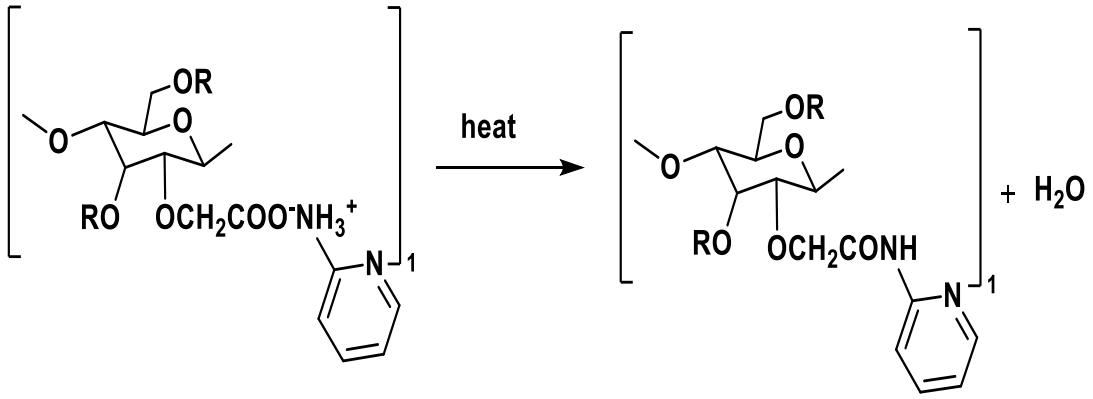
3.1.3 Dehydration of the ammonium carboxylate to produce an amide

Because of low reactivity of the carboxylate ion toward nucleophilic addition-elimination, the reaction does not usually take place in aqueous solution. Scheme 3.3 presents the dehydration reaction that happens due to temperature rise up and helps evaporate water and produces an amide.

Scheme 3.4 shows the conversion of carboxylic group of CMC polymer into amide in one single step without the details illustrated in Schemes 3.2 and 3.3.

Scheme 3.3

Dehydration of ammonium carboxylate to produce amide



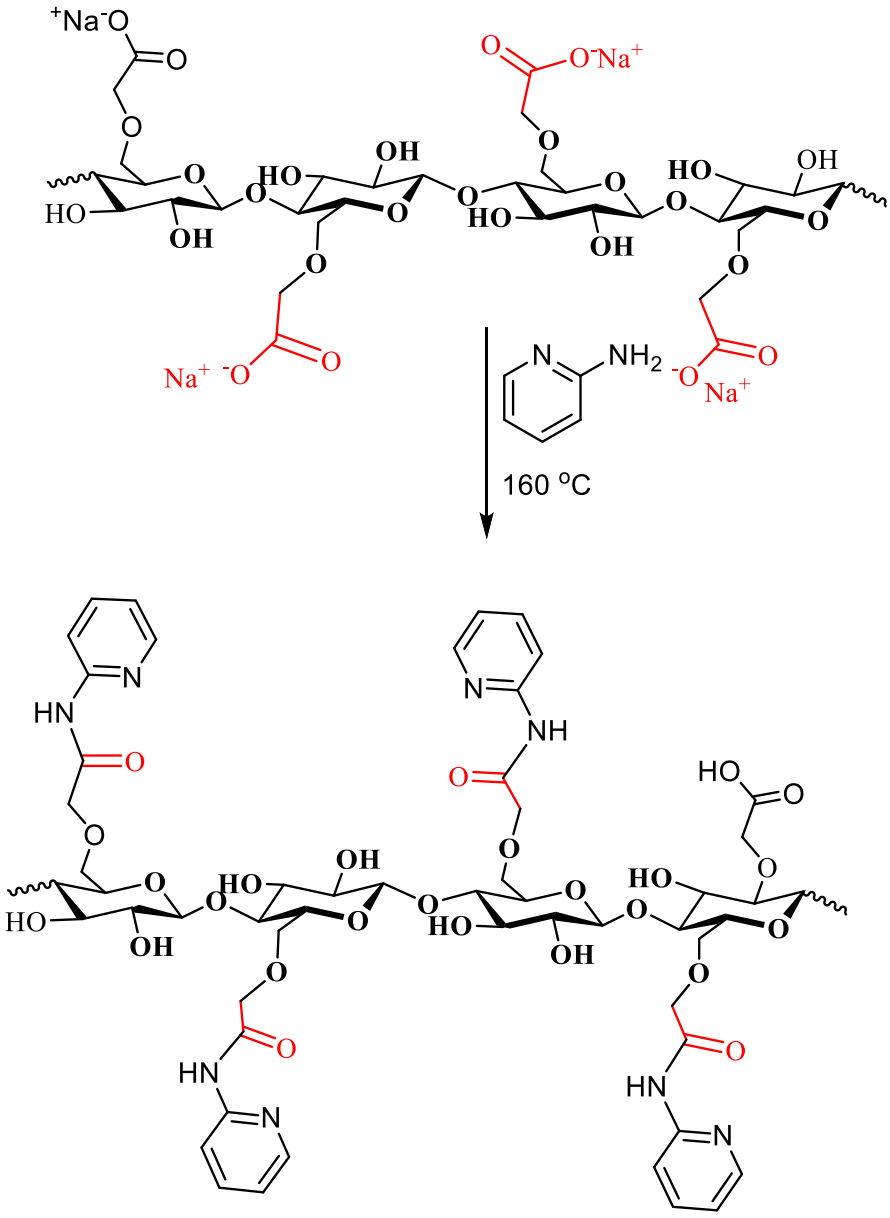
3.1.4 Polymer crosslinking by diethylene triamine

Diethylene triamine (DETA) is one of polyamines that are used as a crosslinking agent for improving the strength and chemical stability of the polymer. As shown in Scheme 3.5. DETA was used to crosslink the CMC-A polymer.

The crosslinking of the polymer is the final step before grinding and washing with methanol, after that the CMC/2-aminopyridine polymer was investigated using various characterization techniques (FT-IR, TGA, AFM…).

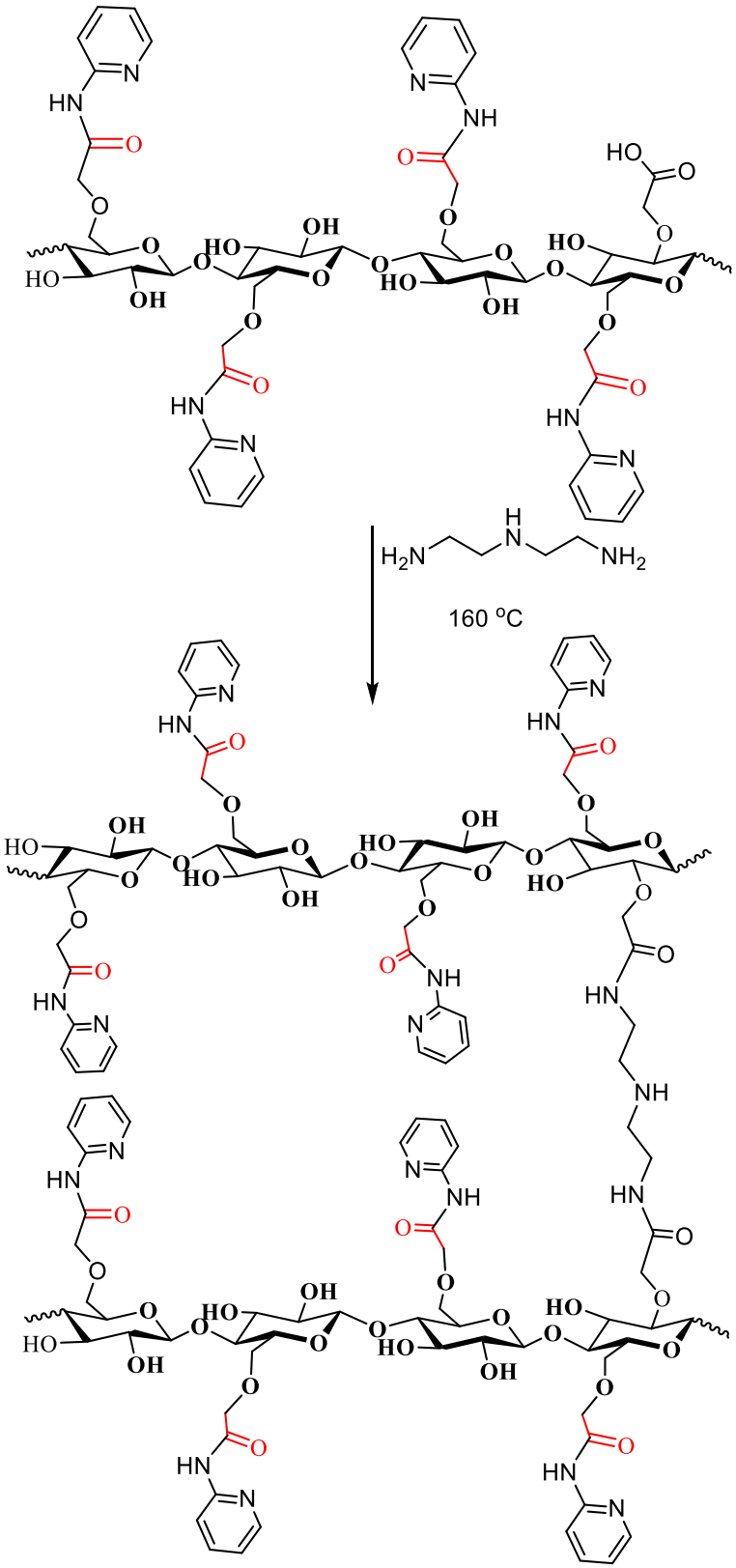
Scheme 3.4

CMC modification by 2-aminopyridine



Scheme 3.5

CMC-A polymer crosslinking



3.1.4.1 FT-IR analysis of the polymer

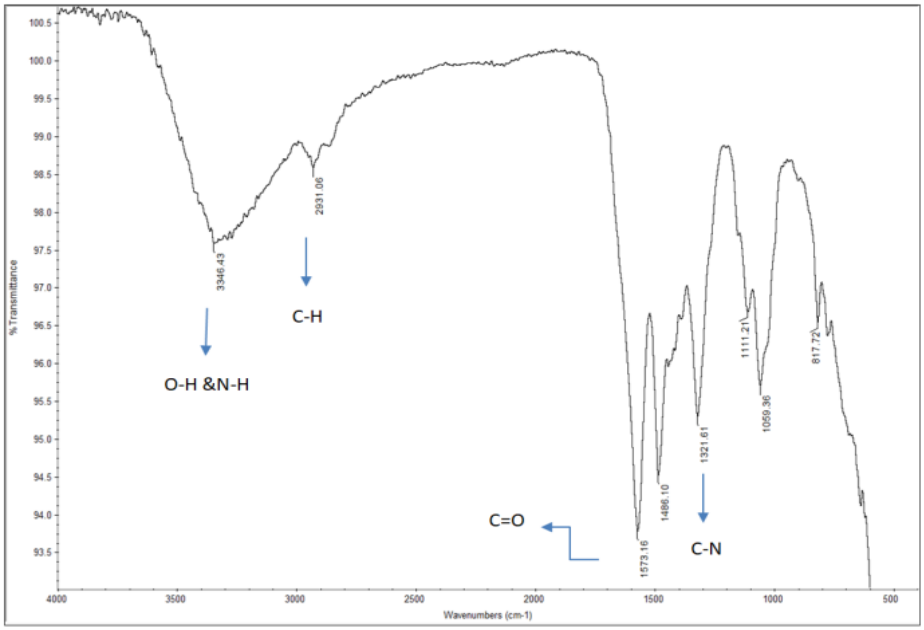
The IR spectrum for the prepared polymer CMC-A is shown in **figure 3.6** which represents the characteristic peaks. It is obvious from the spectral peaks that the prepared polymer has amide functionality which gives it higher affinity toward metal ions due to the presence of nitrogen atoms.

The broad band at 3346 cm^{-1} is related to the (O-H) bond vibration overlapping with (N-H) stretching vibration.

The most intense sharp peak at 1573 cm^{-1} is characteristic of the carboxyl group (C=O) of CMC-A amide group, and the observation of one spike at the C=O peak indicates a secondary amide. The peak at 1321 cm^{-1} is for C-N stretching vibration.

Figure 3.1

IR spectra of the Polymer



3.1.4.2 Thermal gravimetric analysis (TGA) of the polymer

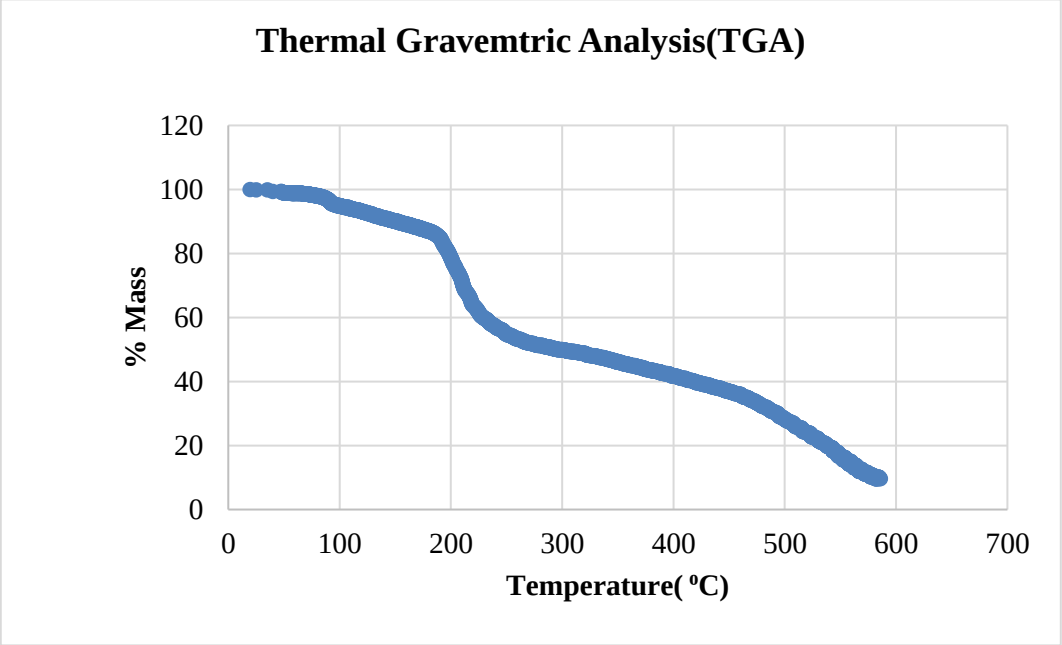
Thermal gravimetric analysis is a useful tool to determine the thermal stability of the prepared polymer at high temperatures by measuring the mass of the polymer sample as a function of temperature.

Figure 3.2 shows the TGA graph that represents how the mass changes with increasing temperature and it is obvious that the CMC-A polymer is relatively stable.

The first mass loss was at temperature equals 190 ºC probably due to decomposition of hydroxyl and carboxyl groups and because the polymer contains more than one functional group, the mass loss happened gradually. The complete decomposition of the polymer occurred at nearly 599 ºC with residual mass of 8.61%.

Figure 3.2

TGA for the CMC-A polymer



3.1.4.3 Atomic Force Microscopy (AFM) for CMC-A polymer

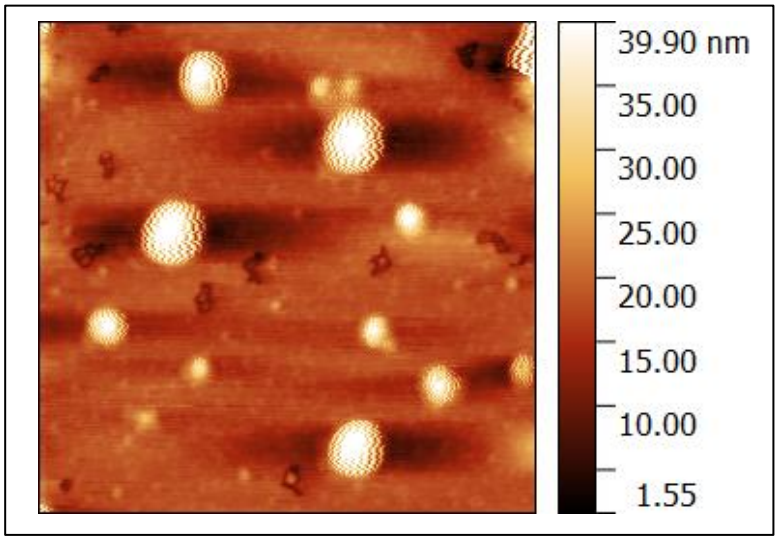
This type of microscopic techniques was used to get information about the surface of the prepared polymer.

in this research AFM was used to form a microscopic image with high resolution of the topography (three-dimensional shape) of CMC-A polymer surface at a high resolution.

Figure 3.3 shows spherical particles of the polymer with diameter size:30-50 nm.

Figure 3.3

AFM image of the CMC-A polymer



3.2 Adsorption Results

In this study, the main purpose is to identify the prepared polymer efficiency for waste water treatment; that is to investigate the adsorption capacity of the polymer toward the toxic heavy metal ion Cu^{2+} according to procedure mentioned above in section 2.4.

The remaining concentration of heavy metal was determined using atomic adsorption spectroscopy. Equilibrium adsorption capacity and removal percentage were calculated to evaluate the performance of the adsorption process according to equations 1 and 2 in section 2.4.3.

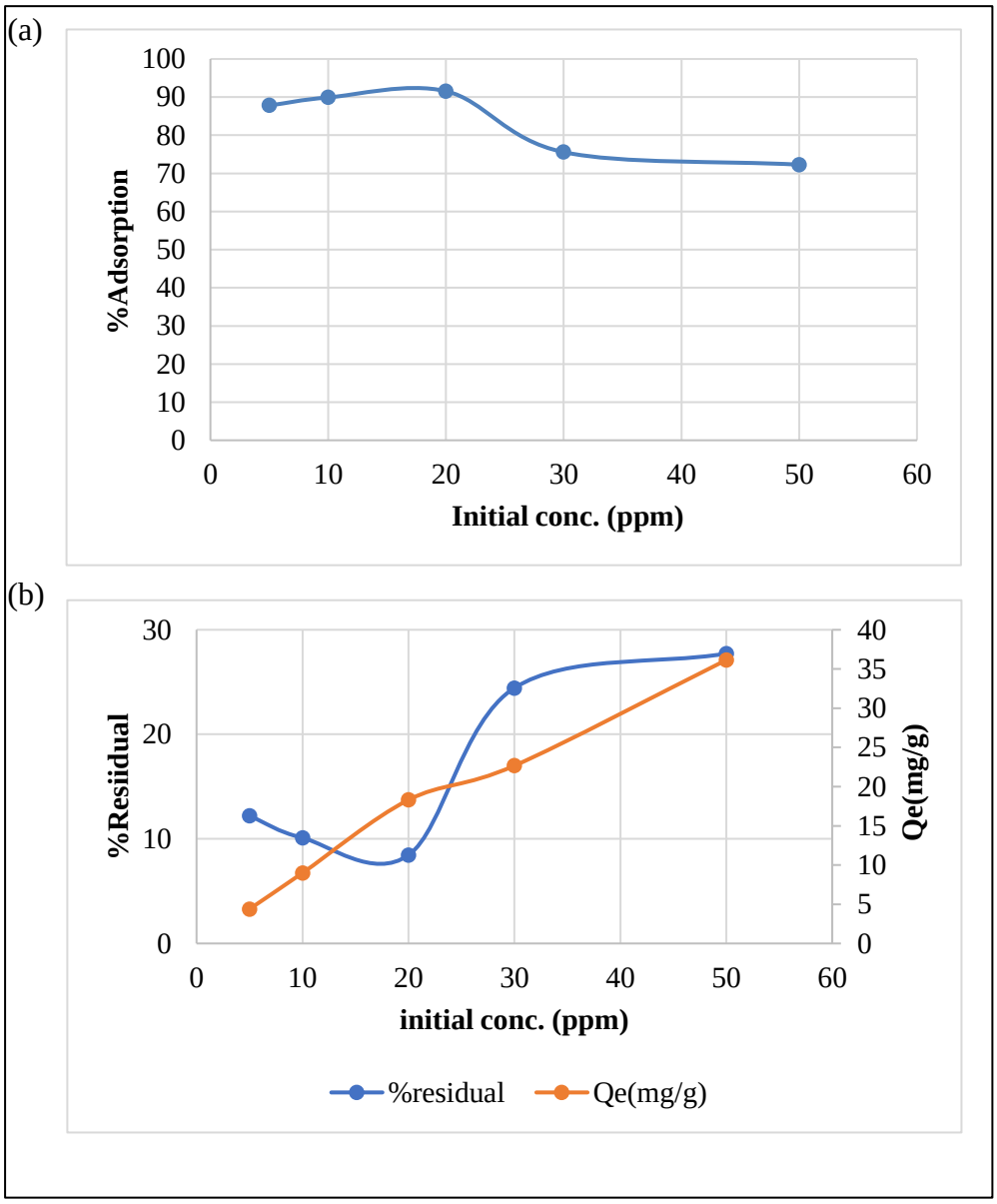
3.2.1 Adsorption of Copper (Cu^{2+}) Ions

3.2.1.1 Effect of Cu^{2+} Initial Concentration

The study of the effect of initial concentration of the metal ion on the adsorption efficiency was performed according to the section 2.4.4 where the Cu^{2+} initial concentration varied in the range (5-50 ppm) and the other parameters kept constant. Figure 3.4 summarizes the results of adsorption percent and adsorption capacity under the effect of initial ion concentration.

Figure 3.4

The effect of initial ion concentration on the adsorption of Cu^{2+} ions



Note: (a) Effect of initial concentration of adsorbate on the Adsorption percentage of Cu^{2+}, (b)Effect of initial adsorbate concentration on the adsorption capacity of Cu^{2+}.

As noticed from Figure 3.4(a), the adsorption percent is concentration dependent, it increases proportionally with increasing the initial concentration of Cu^{2+} up to 20 ppm where the highest adsorption of Cu^{2+} ions was about 91.55% at this concentration (20 ppm). After that, the adsorption percent decreases slightly then held constant approximately and further increase in Cu^{2+} ion concentration leads to insignificant change in adsorption as obvious from the figure.

At first with low concentration of copper ions, the adsorption percent increases rapidly as the initial ion concentration increases and this is continued while there are available active sites on the polymer surface.

Further increase in the concentration of Cu^{2+} ions while the active sites keep unchanged and fixed leads to decrease in adsorption because a lot of ions left in solution without being adsorbed; once all the active sites being occupied and the adsorbent being saturated, the adsorption will reach a plateau and the increase in ion concentration will not lead to increase in adsorption percent [54].

Figure 3.4 (b) shows that capacity of adsorption increases gradually with increasing the initial concentration of the adsorbate and that is because of the presence of a driving force of the mass transfer along with presence of a lot of vacant binding sites, the removal percentage decreases as the vacant sites being limited with increasing the initial concentration.

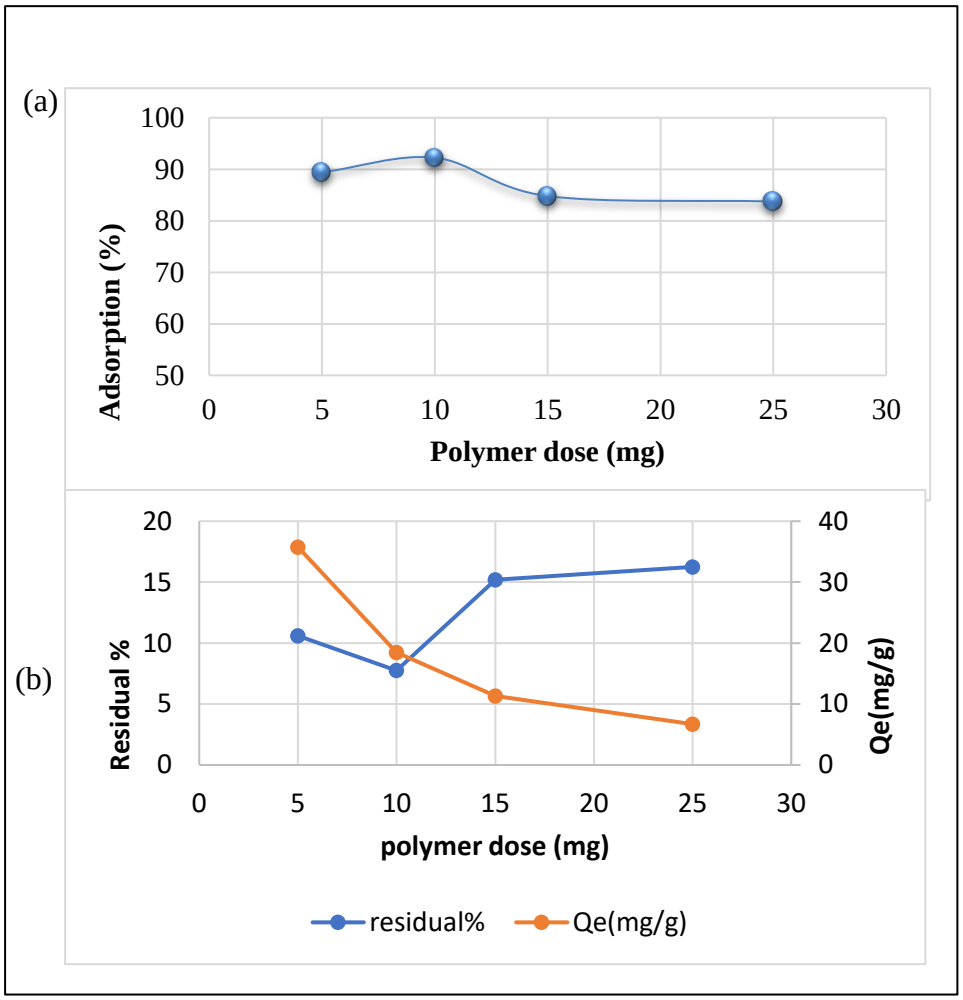
3.2.1.2 Effect of polymer dose

The quantity of the polymer used or the polymer dose gives indication on the available active sites that is essential in the adsorption process. The experiment used to identify the optimum dose that contributes to highest ion removal were discussed in experimental part section 2.4.6 in which the solution of 20 ppm initial concentration of copper ions was used to prepare 4 samples with different polymer dose (5,10,15,25 mg). Other conditions were kept constant.

Figure 3.5 summarizes the results and shows that 10mg of the polymer gives the highest percent removal of 92.25%.

Figure 3.5

The effect of polymer dose on the adsorption of Cu^{2+} ions



Note: (a) Effect of adsorbent dose on %adsorption of Cu^{2+}, (b) Effect of adsorbent dose on adsorption capacity of Cu^{2+}.

Figure 3.5 (a) shows that the removal percentage increases with increasing polymer dosage until certain point and the reason is due to the availability of the vacant sites, but then decreases gradually till reaching a plateau indicating that it reaches equilibrium.

The adsorption capacity decreases with increasing adsorbent dosage as figure 3.5(b) displays, and that is because the unoccupied binding sites that results from increasing adsorbent dosage. Another reason could be the aggregation of particles that results in reducing the total surface area of the polymer, which in its turn decreases the adsorption capacity.

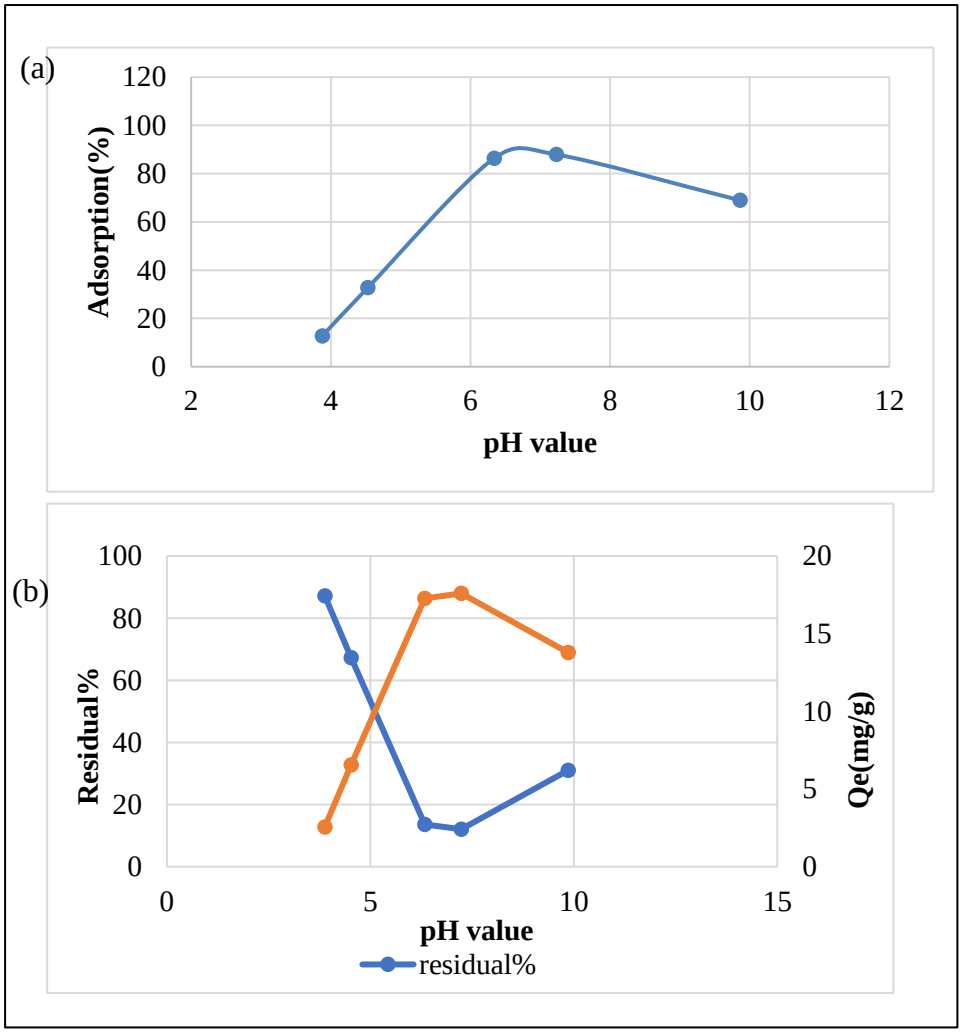
3.2.1.3 Influence of pH on adsorption

The pH value has a crucial effect on the adsorption process. It could affect the protonation of the adsorbent functional groups or the degree of ionization of the adsorbate which in the end affect the interaction of the adsorbent with adsorbate. The experiment that was done to determine the best value of pH for adsorption of copper(II) ions was mentioned in section 2.4.8

Five solutions with pH range (3-10) were investigated keeping other parameters constant (temp = 18 ℃, time = 20 min, polymer dose = 10 mg, conc. = 20 ppm). the results are shown in Figure 3.6

Figure 3.6

The effect of pH value on the adsorption of Cu^{2+} ions



Note: (a) Effect of pH on the % adsorption of Cu^{2+} ion, (b) Effect of pH on % capacity of Cu^{2+}.

The optimum pH value is in the range between 6 and 7 as shown in fig 3.6 (a) and the highest adsorption percent value was 87.93%.

Figure 3.6 (b) illustrates that the adsorption capacity increases with increasing pH value till around 7, after that further increase in pH decreases the adsorption capacity.

It is observed that neither strong acidic nor strong alkali pH is good for adsorption, that is because at high pH value most metals will precipitate where at acidic pH metal ion will compete with the proton in solution to be adsorbed and thus adsorption capacity will decrease [62].

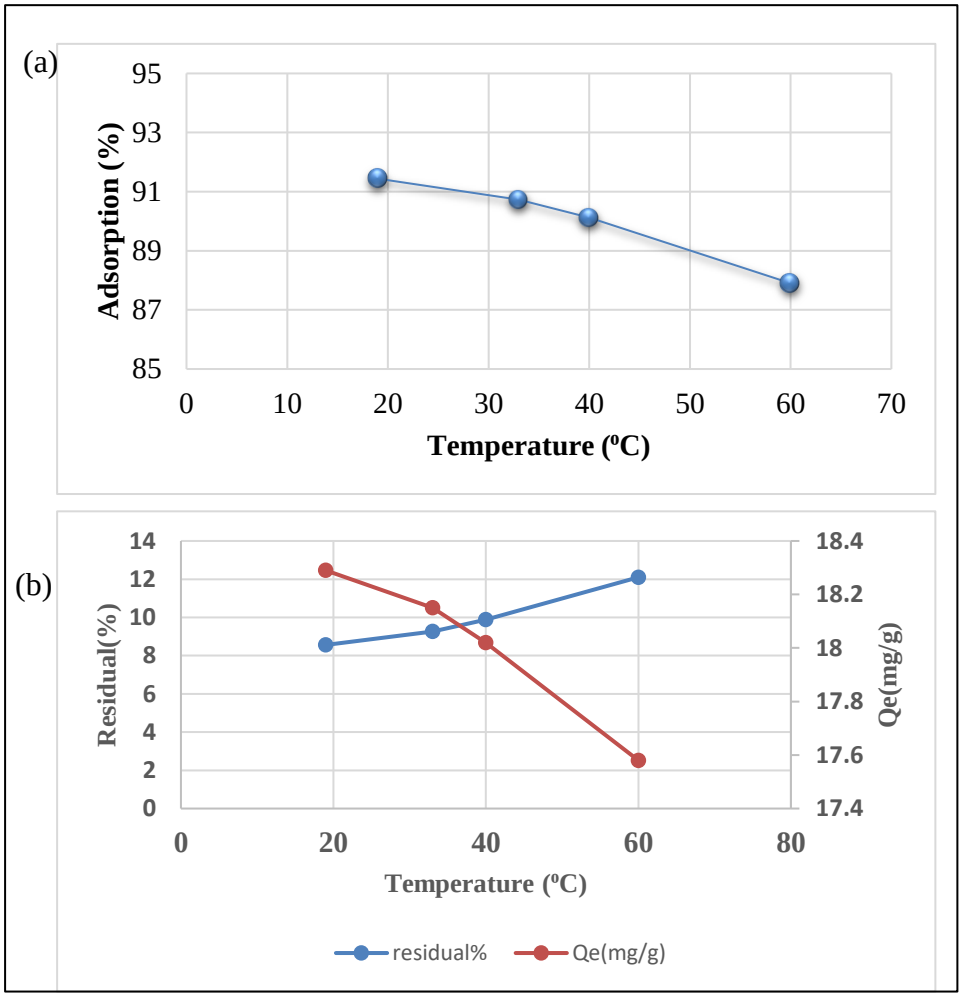
3.2.1.4 Temperature impact on adsorption

The impact of temperature on the adsorption percent and adsorption capacity was investigated in the temperature range 19-60 ºC, the experiment was performed as mentioned earlier in section 2.4.7 where all factors kept constant (conc.20 ppm, dose 10 mg, pH 7.23, time 20 min) for the four samples except the temperature.

Results are shown in figure 3.7 which shows that the highest adsorption value is 91.44% at temperature 19 ºC (room temperature) and the increase in temperature for adsorption process leads to decrease in percent adsorption or removal percent also decrease in the adsorption capacity.

Figure 3.7

The effect of Temperature on the adsorption of Cu^{2+} ions



Note: (a) Effect of Temperature on the % adsorption of Cu^{2+} (b) Effect of temperature on the removal capacity of Cu^{2+}.

Figure 3.7 (a) shows that the relation between temperature and adsorption is inversely proportional, which means that rising temperature leads to decrease percent adsorption.

The adsorption process in which rising temperature results in higher adsorption could considered as endothermic adsorption, however the adsorption process in which rising temperature leads to decrease or inhibit the adsorption performance is exothermic one.

From the figure 3.7 (b) it is apparent that the adsorption capacity decreases with increasing temperature which means that the adsorption of Cu^{2+} ions by CMC-A polymer is a spontaneous and exothermic process.

The reason why adsorption decreases at high temperatures could be the increased kinetic energy of the adsorbate particles which make it likely to not being tied to the adsorbent surface and could easily separate.

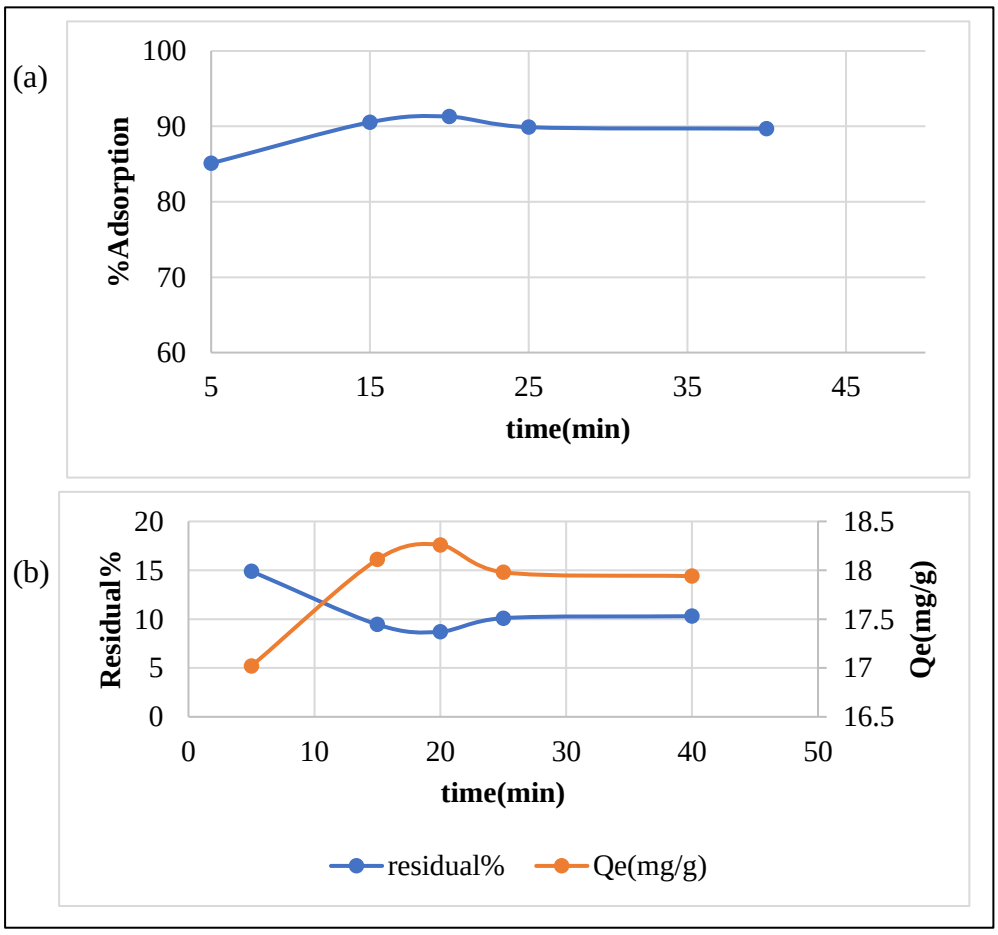
3.2.1.5 Effect of contact time

The experiment that was done to evaluate the time impact, the results are presented in Section 2.4.5 and the influence of adsorption contact time on the removal of copper ions was studied using time values in the range 5-40 minutes.

The results are shown in figure 3.8.

Figure 3.8

The effect of contact time on the adsorption of Cu^{2+} ions



Note: (a) Effect of contact time on the percentage of Cu^{2+} adsorption, (b) effect of contact time on adsorption capacity of Cu^{2+}.

Increasing contact time results in improving the adsorption until reaching certain point at which the equilibrium occurs as shown in figure 3.8 (a). The highest adsorption percent value is 91.3% at 20 minutes time as shown in the figure, then adsorption percent nearly levels off.

At the beginning of the time interval, the capacity of adsorption rises rapidly due to the availability of many vacant binding sites on the surface of the polymer adsorbent as it is obvious from figure 3.8(b), the increase in adsorptive capacity then slows down because the number of vacant sites decreases with time until it levels off when reaching adsorption equilibrium.

The time needed to reach equilibrium is an important indication on the effectiveness of adsorption process, in other words short contact time needed to reach equilibrium means better removal efficiency in reducing the cost of water treatment by treating more volume at the time interval.

3.3 Optimum Adsorption Parameters

The optimum adsorption parameters (time, pH, Temp., dose and concentration) for Cu^{2+} ions are those values contributed to the highest adsorption percentage which is shown in Table 3.1.

Table 3.1

The Optimum Adsorption Parameters for adsorption of copper ions using CMC-A polymer

Parameter	Optimum Value
Contact Time (minute)	20.0
pH value	6 - 7
Temperature (°C)	19.0
Adsorbent Dose (mg)	10 in 10 ml solution
Adsorbate Concentration(ppm)	20 in 10 ml solution

3.4 Adsorption Isotherms

Equilibrium isotherms are useful for giving indication about the adsorbate accumulation on the adsorbent surface. Different models were used in literature but the most important and most common in studying adsorption of heavy metals are the Langmuir and Freundlich models. In this study, these two models were used to find out the capacity of the synthesized polymer in removing copper ions.

Langmuir isotherm assumes that adsorbate particles form a monolayer on the adsorbent surface without side interaction between adsorbate particles themselves. Whereas Freundlich isotherm describe a multi-layer adsorption in which there is interaction between adsorbate molecules.

The correlation coefficient (R^2) decides whether the adsorption of metal ion on the adsorbent polymer is best fitted to Langmuir adsorption model or to Freundlich model [63].

3.4.1 Langmuir adsorption model

In the Langmuir adsorption model all sites on the surface of adsorbent that participate in the adsorption process are homogeneous and has the same energy, and it assumes that each site is being occupied by only one adsorbate particle and these adsorbed particles also does not interact.

The linear form of Langmuir isotherm is represented by Eq.11 in which:

q_e is the concentration of metal ions in equilibrium in the solid phase (mg/g)

C_e illustrates the concentration of metal ions adsorbed in equilibrium per mass of the polymer (ppm),

q_{max} the maximum adsorption capacity (mg/g)

and K_L the Langmuir constant refers to the adsorption energy (l/mg) [64].

$$\frac{\mathbf{1}}{\mathbf{q_e}} = \frac{\mathbf{1}}{(\mathbf{Q_{max}\ K_L\ C_e})} + \frac{\mathbf{1}}{\mathbf{Q_{max}}} \qquad \text{Eq.11}$$

3.4.2 Freundlich isotherm model

Freundlich isotherm model assumes that adsorption happen with heterogeneous multilayer adsorbate particles and there is interaction between adsorbed particles.

Equation 12 represents the formula for Freundlich isotherm.

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \qquad \text{Eq.12}$$

K_f is Freundlich constant (mg/g)

n is another constant (g/L)

n value could be calculated from the y-intercept and slope of Freundlich isotherm graph [64].

Table 3.2 represents the values for both isotherm models, Langmuir and Freundlich

Table 3.2

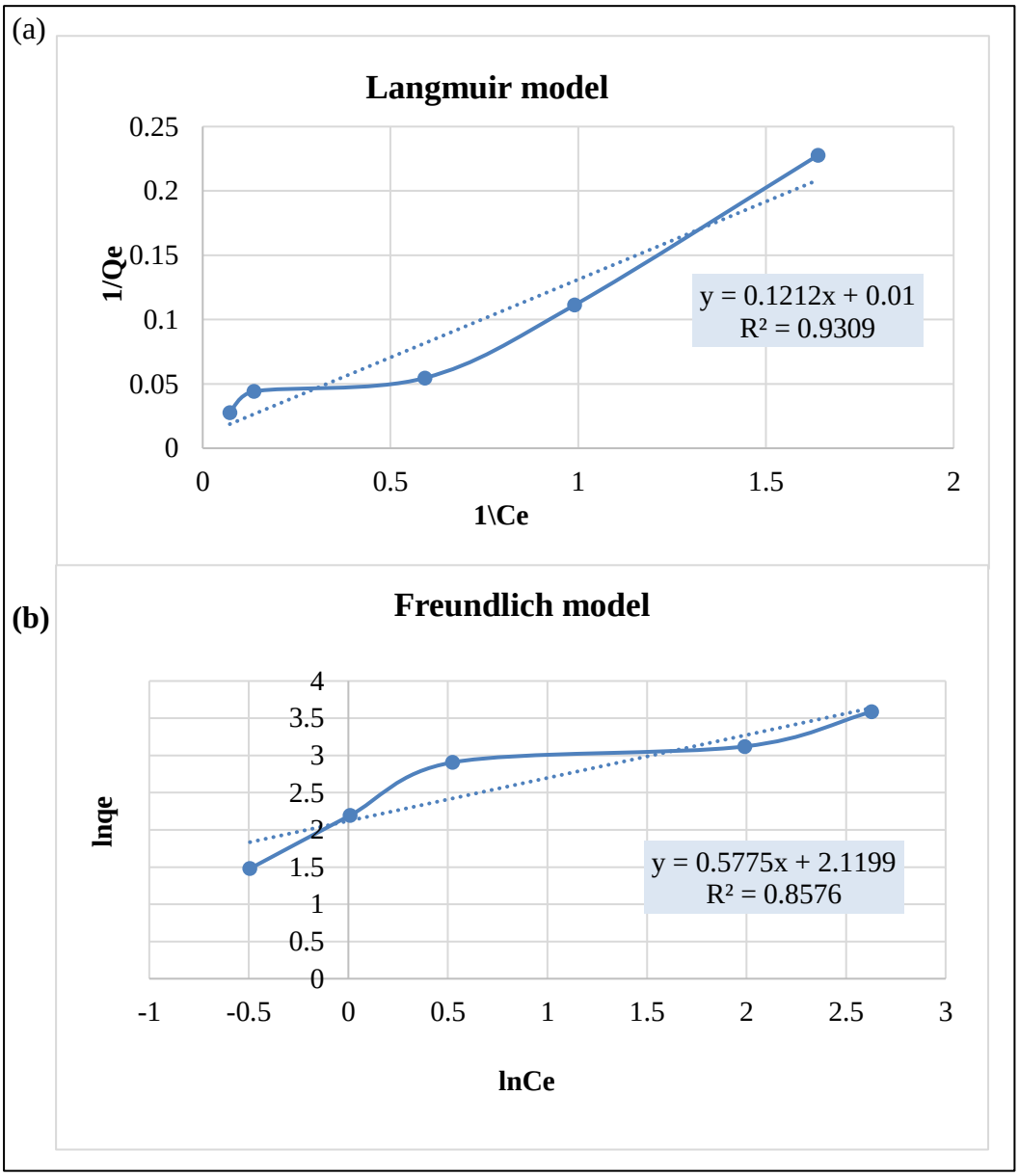
Langmuir and Freundlich model values for Cu^{2+} adsorption by CMC-A polymer

Concentration (ppm) C_i	$[Cu^{2+}]$ (ppm) C_e	Langmuir		Freundlich		lnq_e
		q_e	$1/C_e$	$1/q_e$	lnC_e	
5	0.61	4.39	1.64	0.23	-0.49	1.48
10	1.01	8.99	0.99	0.11	0.01	2.19
20	1.69	18.31	0.59	0.05	0.52	2.91
30	7.33	22.67	0.14	0.04	1.99	3.12
50	13.86	36.14	0.07	0.03	2.63	3.59

Figure 3.9 shows the adsorption isotherm models (both Langmuir and Freundlich) for Cu^{2+} adsorption by CMC-A polymer.

Figure 3.9

Isotherm models for adsorption of Cu^{2+} on CMC-A



Note: (a) Langmuir isotherm model (b) Freundlich isotherm model.

Table 3.3

Langmuir and Freundlich isotherms parameters for CMC-A polymer

Isotherm model	Metal ion	Adsorbent	R^2	Q_{max}	K_L	R_L	N	K_f
Langmuir	Cu^{2+}	CMC-A	0.93	100	0.08	0.38	-	-
Freundlich	Cu^{2+}	CMC-A	0.88	-	-	-	1.73	8.33

The equilibrium parameter (R_L) known as the separation factor can be defined as follows in equation 13.

$$R_L = \frac{1}{1+K_L C_0} = 1 + \frac{\mathbf{1}}{\boldsymbol{K_L C_0}} \qquad \text{Eq. 13}$$

where K_L is the Langmuir constant (L/mg),

and C_0 the initial concentration of copper ions.

The R_L value gives indication about the type of isotherm, and when $R_L > 1$ this means undesirable isotherm, $R_L = 1$ the isotherm is linear, $0 < R_L < 1$ a desirable isotherm and when $R_L = 0$ this means reversible isotherm [64].

As shown from table 3.3, the R_L value is in the range $0 < R_L < 1$ and this is an indication of a favorable shape for the Langmuir isotherm.

Considering both isotherm graphs along with table 3.3 and by comparing R^2 for both isotherms, it is obvious that R^2 for Langmuir is higher and much closer to 1, so the adsorption of copper metal ions by CMC-A obey Langmuir model and the adsorption happens only at the surface.

3.5 Adsorption Kinetics

The rate of adsorption of the metal ions (the adsorbate) from the aqueous solution to the solid adsorbent is well studied by the adsorption kinetics in the form of a line or curve. There are many factors affect the adsorption kinetic include the surface of the adsorbent, the adsorbate concentration and flow rate.

Two models are widely used to study the adsorption kinetics, the pseudo-first order model and the pseudo-second order model [65].

3.5.1 Pseudo-first order model

Pseudo-first order kinetic model is represented by Equation.14 as follows:

$$\ln(q_e - q_t) = lnq_e - K_1 t \qquad \text{Eq.14}$$

q_e: the equilibrium amount of adsorbate per unit weight of adsorbent or it's the adsorption capacity at equilibrium (mg/g).

q_t: the amount of adsorbate per unit weight of adsorbent at a time t (mg/g).

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

3.5.2 Pseudo-second order

The pseudo-second order kinetic model is represented by Equation.15 as follows:

$$\frac{t}{q_t} = \frac{1}{(K_2 q^2)} + \left(\frac{t}{q_e}\right) \qquad \text{Eq.15}$$

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

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

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

Table 3.4 represents the values for both kinetic models, the pseudo first order and the pseudo second order model.

Table 3.4

Values of the pseudo-first order and pseudo-second order kinetic models

Time (min)	$[Cu^{2+}]$ (ppm) C_e	q_t (mg/g)	$\ln(q_e-q_t)$	t/q_t
5	2.98	17.02	0.25	0.29
15	1.89	18.41	-1.6	0.83
20	1.74	18.26	-2.9	1.09
25	2.02	17.98	-1.11	1.39
40	2.06	17.94	-0.99	2.23

Figure 3.10 (in Appendix A) shows (a)the pseudo-first order Model for cu^{2+} adsorption on CMC-A polymer. (b) pseudo-second order model.

If the graph of $\ln(q_e-q_t)$ vs. time gives a straight line with R^2 close to 1, this means that adsorption obeys pseudo-first order kinetic model.

Whereas the adsorption process obeys this model, the pseudo-second order if the plot of (t/q_t) versus (t) gives a straight line with high R^2 value close to 1.

Table 3.5 demonstrates both kinetic parameters for adsorption, pseudo-first order and pseudo second order models.

Table 3.5

Kinetic parameters for the adsorption of cu^{2+} on CMC-A

Kinetic model	Metal ion	R^2	Theo. q_e	Exp. q_e	K_1	K_2
Pseudo-first order	Cu^{2+}	0.063	0.45	18.31	0.022	-
Pseudo-second order	Cu^{2+}	0.99	18.02	18.31	-	1.09

The best way to determine which kinetic model, apply on the adsorption of Cu^{2+} by CMC-A polymer is by comparing the R^2 values of the two models, it is clear that R^2 value is much higher for the pseudo-second order model (0.99) than R^2 for the pseudo-first order model (0.063) as shown in table 3.5 and that means the adsorption of Cu^{2+} ions by the CMC-A polymer follows pseudo-second order kinetics.

There is another indication about the kinetic model, the theoretical value of q_e also confirms that the adsorption process obeys pseudo-second order kinetics because it is close to the experimental value in case of the pseudo-second order model, whereas the theoretical q_e value for pseudo-first order model is (0.45), which is extremely far from the experimental value (18.31).

3.6 Thermodynamics of Adsorption by CMC-A Polymer

Gibbs free energy ΔG^o, enthalpy ΔH^o and entropy ΔS^o are thermodynamic parameters that can be calculated from the following equations [66].

$$K_c = \frac{Q_e}{C_e} \qquad \text{Eq.16}$$

Where:

K_c: equilibrium constant of thermodynamics. (L/g)

Q_e: the amount of metal ion adsorbed at equilibrium per unit adsorbent (mg/g).

$C_{e:}$ is the equilibrium concentration of metal ion in solution (mg/ L).

$$\Delta G° = -RTlnk_c \qquad \text{Eq.17}$$

Where:

R: the universal gas constant (8.314 J/mol/K).

T: the temperature of the solution (K).

$$lnk_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad \text{Eq.18}$$

Plotting $\boldsymbol{lnk_c}$ Vs (1/T) will give the Van't-Hoff plot with slope equals to (-ΔH°/R) and y-intercept equals (ΔS°/R).

Table 3.6 (in appendix A) shows the Thermodynamic values for Van't Hoff plots.

Figure 3.11 (in Appendix B) shows The Van't Hoff plot for Cu^{2+} adsorption on CMC-A.

Table 3.7 (in appendix A) shows the thermodynamic parameters of Cu^{2+} adsorption on CMC-A polymer.

Negative values of ΔG^o calculated in table 3.7 give an indication that the adsorption process is spontaneous. And the degree of spontaneity of the reaction increases with increasing temperature. The adsorption of Cu^{2+} ions by CMC-A polymer decreases with increasing temperature making the adsorption an exothermic process as the negative value of enthalpy change predicts [67].

Negative value of ΔS° means the process of adsorption happens spontaneously at low temperatures which support our finding that the optimum temperature for Cu^{2+} adsorption is 19 ^oC.

3.7 Adsorption on a Real Samples of Sewage

ICP-MS was used to determine the concentration of heavy metal ions present in a sample of sewage water before and after treating with the CMC-A polymer as mentioned in sec. 2.8. The results are tabulated in table 3.8

It is shown in the table that the CMC-A polymer has high efficiency in removing many of the most toxic heavy metals. The adsorption percent for Ag, Cd, Cr, Cu and Pb were 73.01%, 98.05%, 81.31%, 96.66% and 91.79% respectively.

Table 3.8 (in appendix A) shows the ICP-MS analysis results for toxic metal concentrations adsorbed by CMC-A polymer.

3.8 Conclusion

Toxic heavy metal ions have been unconsciously released to the environment and more specifically to the water.

Biological life has been under serious threat worldwide because of water pollution, so that huge efforts are needed to continue doing researches on waste water treatment.

In the current work, CMC with amide functionality was prepared and tested as adsorbent polymer for Cu^{2+} metal ions removal from waste water. The presence of amide functionality (nitrogen atoms) gives the polymer higher affinity toward binding metal ions. CMC-A polymer was synthesized by a rection between carboxymethyl cellulose and 2-aminopyridine then crosslinking by DETA. The prepared polymer was characterized using FT-IR, AFM and TGA. Efficiency of adsorption was investigated under various factors of temperature, time, initial concentration, polymer dose and pH value.

It has been found that the prepared polymer was able to adsorb Cu^{2+} ions with percent adsorption 92.25% at pH range (6-7), polymer dose of 10 mg, initial metal concentration 20 ppm at temperature 19 ºC for 20 minutes contact time. Thermodynamic parameters revealed that the adsorption process is exothermic ($\Delta H° < 0$), spontaneous ($\Delta G° < 0$), and spontaneous at low temperatures ($\Delta S° < 0$).

The adsorption process was following the pseudo second order kinetic model ($R^2 = 0.99$) and matched with the Langmuir isotherm ($R^2 = 0.93$).

3.9 Recommendations

1. The CMC-A polymer could be used in water treatment from other toxic metals like Ag, Pb, Cr and others ions.
2. The CMC-A polymer could be used in different researches other than water treatment, such as in biomedical engineering and drug delivery.
3. The polymer itself could undergo some alteration or developments to enhance the adsorption ability by changing the functional groups.

List of Abbreviations

Abbreviation	Meaning
WHO	World Health Organization
AC	Activated Carbon
AOPs	Advanced Oxidation Processes
EPA	Environmental Protection Agency
GO	Graphene Oxide
CNTs	Carbon Nanotubes
MOF	Metal Organic Framework
nZVI	Nanoscale Zero Valent Iron
AGU	Anhydro Glucopyranose
DP	Degree of Polymerization
CNC	Cellulose Nanocrystalline
DS	Degree of Substitution
CMC	Carboxymethylcellulose
DETA	Diethylene triamine
FT-IR	Fourier-Transform Infrared Spectrophotometer
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
AFM	Atomic Force Microscopy
FAAS	Flame Atomic Adsorption Spectrometer
TGA	Thermal Gravimetric Analysis
CMC-A	Carboxymethyl cellulose/2-aminopyridine polymer
C_0	Initial Concentration of metal ion (mg/L)
C_e	Equilibrium concentration of metal ion (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_L	Langmuir constant
K_F	Freundlich constant
K_1	Pseudo-first order rate constant
K_2	Pseudo-second order rate constant
K_c	The thermodynamic constant

E_a	Activation energy
Δ H°	The change in enthalpy
Δ S°	The change in entropy
Δ G°	The change in Gibbs free energy
R	The universal gas constant
T	The Absolut temperature
1/n	Dimensionless Freundlich constant
R_L	Separation factor dimensionless constant

References

1. Kılıç, Z. *The importance of water and conscious use of water*. Int J Hydro. 2020; 4(5):239-241.

2. Li, P. and Wu, J. *Drinking water quality and public health*. Exposure and Health. 2019; 11(2): 73-79.

3. Zamora-Ledezma, C. et al. *Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods*. Environmental Technology & Innovation. 2021; 22: 101504.

4. Haseena, M. et al. *Water pollution and human health*. Environ Risk Assess Remediat. 2017;1(3):16-19.

5. Ahmed, S. and Ismail, S. *Water pollution and its sources, effects & management: a case study of Delhi*. International Journal of Current Advanced Research. 2018; 7(2): 10436-10442.

6. Voulvoulis, N. *Water reuse from a circular economy perspective and potential risks from an unregulated approach*. J.C.O.i.E.S. and Health. 2018; 2: 32-45.

7. Fatta-Kassinos, D., Dionysiou, D.D and Kümmerer, K. *Advanced treatment technologies for urban wastewater reuse*. Springer. 2016; 45.

8. Dong, Z. et al. *Recovery of Au (III) by radiation synthesized amino methyl pyridine functionalized adsorbents based on cellulose.* Chemical Engineering Journal. 2016; 283: 504–513.

9. Fu, F. and Wang Q. *Removal of heavy metal ions from wastewaters: A review*. Journal of Environmental Management. 2011; 92: 407-418.

10. Zhou, Q. et al. *Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017*. Global ecology and conservation. 2020; e00925.

11. Brescia, S. *Thresholds of adversity and their applicability to endocrine disrupting chemicals*. C.R.i.T. 2020; 50(3): 213-218.

12. Lawal, K.K. et al. *A review on the public health implications of heavy metals*. 2021; 10(3): 255-265.

13. Jaishankar, M. et al. *Toxicity, mechanism and health effects of some heavy metals.* Interdisciplinary Toxicology. 2014; 7(2): 60-72.

14. Borobia, M. et al. *Copper Poisoning, a Deadly Hazard for Sheep*. Animals. 2022; 12(18): 2388.

15. . Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Copper. Atlanta, GA: Centers for Disease Control; 2002.

16. Tchounwou, P.B. et al. *Heavy metal toxicity and the environment*. 2012; 101: 133-164.

17. Dorsey, A. et al. *Toxicological Profile for Copper*. (ATSDR). 2002

18. Tchounwou, P.B. Newsome, C. Williams, J. Glass K. *Copper-induced cytotoxicity and transcriptional activation of stress genes in human liver carcinoma cells*. Metal Ions Biol Med. 2008; 10: 285–290.

19. USEPA. *Drinking Water Requirements for States and Public Water Systems*: Lead and Copper Rule. 2008.

20. Muslim, A. et al. *Silicified coal adsorbents for adsorption of Cu (II) from the aqueous Solution: Non-Linear kinetic and isotherm studies.* Materials Today: Proceedings. 2022; 63: S400–S405.

21. Kavitha, C. et al. *Elimination of Lead by Biosorption on Parthenium stem powder using Box-Behnken Design*. South African Journal of Chemical Engineering. 2022; 42: 270-279.

22. Moreno-Castilla, C. *Adsorption of organic molecules from aqueous solutions on carbon materials.* Carbon. 2004; 42(1): 83-94.

23. Fu, F. and Wang Q. *Removal of heavy metal ions from wastewaters: A review*. Journal of Environmental Management. 2011; 92: 407-418.

24. Ahn, C.K., Park, D., Woo, S.H. and Park, J.M. *Removal of cationic heavy metal from aqueous solution by activated carbon impregnated with anionic surfactants*. Journal of hazardous materials. 2009; 164: 1130–1136.

25. Tamjidi, S. and Ameri, A. *A review of the application of sea material shells as low cost and effective bio-adsorbent for removal of heavy metals from wastewater*. Environ Sci Pollut Res. 2020; 27(25): 31105-31119.

26. Larous, S., Meniai, A.H. and Lehocine M. *Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust*. Desalination. 2005; 185: 483–490.

27. Sophia A. and Lima E.C. *Removal of emerging contaminants from the environment by adsorption*. Ecotoxicology and Environmental Safety. 2018; 150: 1–17.

28. Wang, Li. et al. *Rational design, synthesis, adsorption principles and applications of metal oxide adsorbents: a review*. Nanoscale. 2020; 12(8): 4790-4815.

29. Dong, Z. et al. *Recovery of Au (III) by radiation synthesized amino methyl pyridine functionalized adsorbents based on cellulose.* Chemical Engineering Journal. 2016; 283: 504–513.

30. Mo, J. et al. *A review on agro-industrial waste (AIW) derived adsorbents for water and wastewater treatment*. Journal of environmental management. 2018; 227: 395-405.

31. Chakraborty, R. et al. *Adsorption of heavy metal ions by various low-cost adsorbents: a review*. International Journal of Environmental Analytical Chemistry. 2022; 102(2): 342-379.

32. Kumar, R. and Sharma, R.K. *Synthesis and characterization of cellulose based adsorbents for removal of Ni (II), Cu (II) and Pb (II) ions from aqueous solutions*. Reactive and Functional Polymers. 2019; 140: 82–92.

33. Suhas et al. *Cellulose: A review as natural, modified and activated carbon adsorbent*, Bioresource Technology. 2016; 216: 1066–1076.

34. Malin, W. et al. *Cellulose and the role of hydrogen bonds: not in charge of everything*. Cellulose. 2022; 29: 1–23.

35. Demirbas, A. *Heavy metal adsorption onto agro-based waste materials: A review*. Journal of Hazardous Materials. 2008; 157: 220–229.

36. Peng, B.L. et al. *Chemistry and applications of nanocrystalline cellulose and its derivatives: a nanotechnology perspective*. THE CANADIAN JOURNAL OF CHEMICAL ENGINEERING. 2011; 89(5): 1191-1206.

37. YOUNG, R. *CROSS-LINKED CELLULOSE AND CELLULOSE DERIVATIVES*, Absorbent Technology. 2002;(): 233-277.

38. Saravanan, R. and Ravikumar, L. *The Use of New Chemically Modified Cellulose for Heavy Metal Ion Adsorption and Antimicrobial Activities*. Journal of Water Resource and Protection. 2015; 7: 530-545.

39. Shen, W. et al. *Adsorption of Cu (II) and Pb (II) onto diethylenetriamine-bacterial cellulose*, Carbohydrate Polymers. 2009; 75: 110-114.

40. Ji, F. et al. *Preparation of cellulose acetate/zeolite composite fiber and its adsorption behavior for heavy metal ions in aqueous solution*. Chemical Engineering Journal. 2012; 209: 325-333.

41. Nguyen, T. et al. *Thiosemicarbazone-Modified Cellulose: Synthesis, Characterization, and Adsorption Studies on Cu (II) Removal*. ACS Omega. 0c01129.

42. Qin, F. et al. *Efficient Removal of Cu2+ in Water by Carboxymethylated Cellulose Nanofibrils: Performance and Mechanism*. Biomacromolecules. 2019; 20(12): 4466-4475.

43. Rahman, M. S. et al. *Recent Developments of Carboxymethyl Cellulose*. Polymers. 2021; 13: 1345.

44. Salama, A., Etri, S., Mohamed, S. and El-Sakhawy, M. *Carboxymethyl cellulose prepared from mesquite tree: new source for promising nanocomposite materials*. Carbohydr. Polym. 2018; 189: 138–144.

45. Manzoor, K.; Ahmad, M.; Ahmad, S.; Ikram, S. *Removal of Pb (ii) and Cd (ii) from wastewater using arginine cross-linked chitosan–carboxymethyl cellulose beads as green adsorbent*. RSC Adv. 2019; 9: 7890–7902.

46. Wei, W.; Kim, S.; Song, M.-H.; Bediako, J.K.; Yun, Y.-S. *Carboxymethyl cellulose fiber as a fast binding and biodegradable adsorbent of heavy metals*. J. Taiwan Inst. Chem. Eng. 2015; 57: 104–110.

47. Gasemloo, S.; Khosravi, M.; Sohrabi, M.R.; Dastmalchi, S.; Gharbani, P. *Response surface methodology (RSM) modeling to improve removal of Cr (VI) ions from tannery wastewater using sulfated carboxymethyl cellulose nano filter*. J. Clean. Prod. 2018; 10: 177.

48. Gosselin, R.E.; Smith, R.P. and Hodge. H.C. *Clinical Toxicology of Commercial Products*. Journal of pharmaceutical sciences. 1985; 74(10): 1139-1139.

49. Bu¨yu¨kmurat, Y.; Akalin, E.; O¨ zel, A.E.; Akyu¨z, S. *Calculation and analysis of IR spectrum of 2-aminopyridine*. Journal of Molecular Structure. 1999; 482–483: 579–584.

50. Monier, M.; Ayad, D.M.; Abdel-Latif, D.A. *Adsorption of Cu (II), Cd (II) and Ni (II) ions by cross-linked magnetic chitosan-2-aminopyridine glyoxal Schiff's base*. Colloids and Surfaces B: Biointerfaces. 2012; 94: 250–258.

51. Zheng, M. et al. *2-aminopyridine functionalized magnetic core–shell Fe3O4@polypyrrole composite for removal of Mn (VII) from aqueous solution by double-layer adsorption*. Separation and Purification Technology. 2021; 277: 119455.

52. Zhang, Y.; Chen, Y.; Wang, C.; Wei, Y. *Immobilization of 5-aminopyridine-2-tetrazole on cross-linked polystyrene for the preparation of a new adsorbent to*

remove heavy metal ions from aqueous solution. Journal of Hazardous Materials. 2014; 276: 129–137.

53. Viana, M.M. et al. *Microwave-assisted synthesis of polyacrylamide-aminated graphene oxide hybrid hydrogel with improved adsorption properties*. Journal of Environmental Chemical Engineering. 2020; 8: 104415.

54. Moyo, M. et al. *Adsorption batch studies on the removal of Pb (II) using maize tassel based activated carbon*. Journal of Chemistry. 2013; 2013: 8.

55. Zahoor, M. *Removal of pesticides from water using granular activated carbon and ultrafiltration membrane—a pilot plant study*. Journal of Encapsulation and adsorption sciences. 2013; 2013(3): 71-76.

56. Sud, D., Mahajan G., and Kaur, M.P. *Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions–A review*. Bioresource technology. 2008; 99(14): 6017-6027.

57. Hamed, O. et al. *Synthesis of a cross-linked cellulose-based amine polymer and its application in wastewater purification*. Environmental Science and Pollution Research. 2019; 26(27): 28080-28091.

58. Potgieter, J., Pearson S., and Pardesi C. *Kinetic and thermodynamic parameters for the adsorption of methylene blue using fly ash under batch, column, and heap leaching configurations.* CCGP. 2018; 10(2): 23-33.

59. Anirudhan, T.S. and Radhakrishnan, P.G. *Thermodynamics and kinetics of adsorption of Cu (II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell*. J. Chem. Thermodynamics. 2008; 40(4): 702-709.

60. Mustapha, S. et al. *Adsorption isotherm, kinetic and thermodynamic studies for the removal of Pb (II), Cd (II), Zn (II) and Cu (II) ions from aqueous solutions using Albizia lebbeck pods*. Applied Water Science. 2019; 9: 142.

61. Moyo, M. et al. *Adsorption Batch Studies on the Removal of Pb (II) Using Maize Tassel Based Activated Carbon.* journal of chemistry.2013;10(1155):8.

62. Liu, L. et al. *Application of nanotechnology in the removal of heavy metal from water*. Elsevier. 2019; 10(1016): 83-147.

63. Anirudhan, T.S. and. Sreekumari, S.S. *Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons*. J.o.E.S 2011; 23(12): 1989-1998.

64. Ebrahimi, F. et al. *Fabrication of nanofibers using sodium alginate and Poly (Vinyl alcohol) for the removal of Cd^{2+} ions from aqueous solutions: Adsorption mechanism, kinetics and thermodynamics.* Heliyon. 2019; 5(11): e02941.

65. Kajjumba, G.W. et al. *Modelling of adsorption kinetic processes—errors, theory and application.* 2018: 10(5772): p. 1-19.

66. Kumar, P.S. and Gayathri, R. *Adsorption of Pb2+ ions from aqueous solutions onto bael tree leaf powder: isotherms, kinetics and thermodynamics study.* J.E.S.T. 2009. 4(4): 381-399.

67. Boparai, H.K., Joseph, M. and O'Carroll, D.M. *Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles.* J.o.h.m. 2011; 186(1): 458-465.

Appendices

Appendix A

Tables

Table 3.6

The Thermodynamic values for Van't Hoff plots

Temperature (℃)	$[Cu]^{2+}$ (ppm) C_e	1/T (K^{-1})	lnK_c
19	1.71	0.0034	2.37
33	1.85	0.0033	2.28
40	1.98	0.0032	2.21
60	2.42	0.003	1.98

Table 3.7

The thermodynamic parameters of Cu^{2+} adsorption on CMC-A polymer

Metal ion	Temp.(K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol.K)
Cu^{2+}	292.15	-4.83	-7.75	-0.01
	306.15	-4.69		
	313.15	-4.62		
	333.15	-4.42		

Table 3.8

The ICP-MS analysis results for toxic metal concentrations adsorbed by CMC-A polymer

Analyte	Conc. Before (ppb)	Mean conc. After (ppb)	Adsorption%
Ag	0.96	0.26	73.01
Al	222.70	97.33	56.29
As	13.74	7.66	44.24
B	280.53	116.36	58.52
Ba	49.52	22.72	54.12
Be	0.04	0.00	100.00
Bi	4.72	1.06	77.61
Cd	2.36	0.05	98.05
Co	1.90	1.21	36.58
Cr	1390.52	259.88	81.31
Cu	331.43	11.08	96.66
Ga	0.81	0.63	21.82
Li	22056.80	9.22	99.96

Mn	109.38	40.77	62.72
Mo	2.96	1.62	45.30
Ni	17.34	11.32	34.74
Pb	10.60	0.87	91.79
Rb	88.46	34.23	61.30
Se	20.60	4.13	79.95
Te	0.77	0.16	78.95
Tl	0.09	0.01	85.71
U	0.21	0.16	26.19
V	35.68	21.46	39.86
Zn	59.60	35.06	41.18

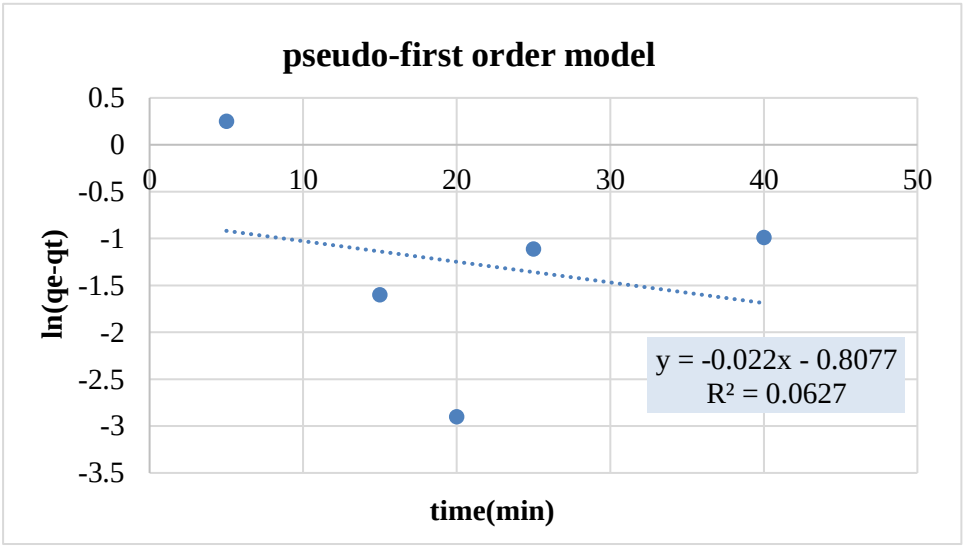
Appendix B

Figures

Figure 3.10

(a) The pseudo-first order Model for cu²⁺ adsorption on CMC-A polymer. (b) pseudo-second order model

(a)



(b)

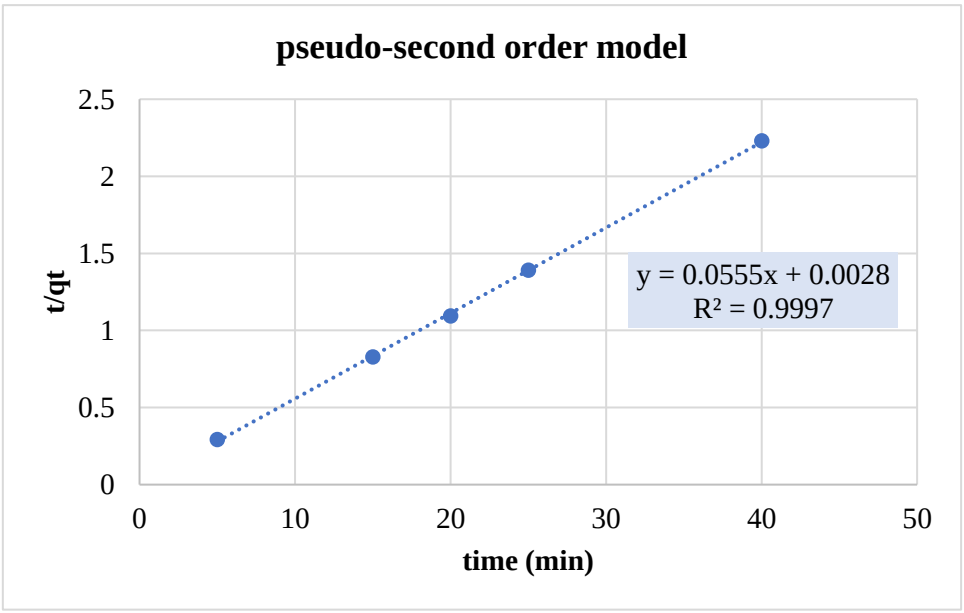
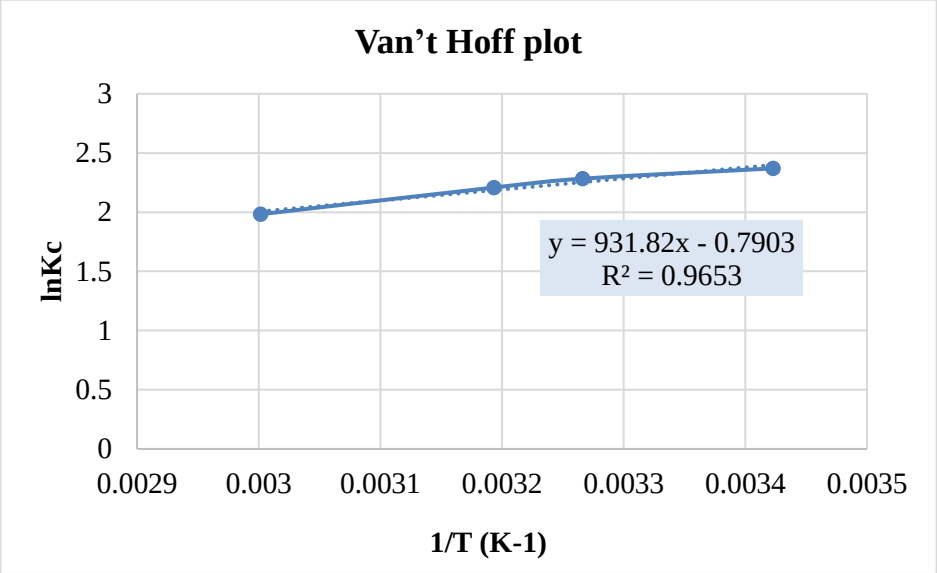


Figure 3.11

The Van't Hoff plot for Cu^{2+} adsorption on CMC-A



جـامعـــة النجاح الوطنية

كليـــة الدراســـات العليـــا

السيليولوز المتشابك مع المواقع التناسقية ثلاثية الارتباط: التحضير والتطبيق في استخلاص الأيونات السامة من مياه الصرف الصحي

إعداد

شهد هاني محمود شاهين

إشراف

د. إبراهيم أبو شقير

أ. د. عثمان حامد

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

2023

السيليولوز المتشابك مع المواقع التناسقية ثلاثية الارتباط: التحضير والتطبيق في استخلاص الأيونات السامة من مياه الصرف الصحي

إعداد

شهد هاني محمود شاهين

إشراف

د. إبراهيم أبو شقير

أ. د. عثمان حامد

الملخص

الخلفية: يعتبر تلوث المياه الذي يأتي من التصنيع والتحضر السريع مشكلة خطيرة لأن المياه هي واحدة من الموارد الحيوية للحياة، وهي مهمة لجميع البشر والبيئة والمجتمع والاقتصاد.

تعتبر المعادن الثقيلة مثل: (Ag, Hg, Pb, Cr, Cu) من بين الملوثات التي هي مصدر قلق رئيسي وتحتاج إلى إزالتها من مياه الصرف الصحي بواسطة تقنيات مختلفة تشمل الامتزاز كعملية معالجة مستخدمة على نطاق واسع. تعتبر الممتزات منخفضة التكلفة والفعالة من البوليمرات الطبيعية ذات أهمية كبيرة لإزالة المعادن الثقيلة من مياه الصرف الصحي وقد تم توجيه الأبحاث نحو تعديل هذه الممتزات الطبيعية لتعزيز كفاءة الامتصاص.

الهدف: الهدف الرئيسي من هذا العمل هو تحضير بوليمر كربوكسي ميثيل السليلوز المتشابك مع 2-أمينوبيريدين من أجل جعله رابطا ممتازا للمعادن الثقيلة لتطبيقه في تنقية مياه الصرف الصحي.

المنهجية: تبدأ طريقة تحضير البوليمر بتفاعل بين بوليمر CMC و2-aminopyridine لتحويل المجموعة الكربوكسيلية إلى أميد ثم ربط البوليمر المحضر بواسطة DETA لمزيد من الاستقرار. تم تحليل البوليمر الناتج بواسطة FT-IR وAFM وTGA.

النتائج: تم فحص النسبة المئوية لإزالة أيون Cu2+ بواسطة البوليمر المحضر تحت تأثير المتغيرات التالية: درجة الحرارة والوقت ودرجة الحموضة وتركيز المعدن الابتدائي وتركيز البوليمر. الحد الأقصى لإزالة Cu^{2+} بواسطة بوليمر CMC–A هو 91.55٪ عند درجة الحموضة 7.23، درجة الحرارة 19 درجة مئوية، الوقت 20 دقيقة، تركيز الايون 20 جزء في المليون وتركيز البوليمر 10 جزء في المليون. تم فحص متساوي الحرارة والامتزاز والحركية والديناميكا الحرارية لتحديد آلية وعفوية عملية الامتزاز وكشفت النتائج أنها طاردة للحرارة ($\Delta H^\circ < 0$) وعفوية ($\Delta G^\circ < 0$) وتحدث تلقائيا في درجات حرارة منخفضة .($\Delta S^\circ < 0$) يتبع الامتزاز نموذج الترتيب الثاني الزائف مع ($R2 = 0.99$) وتم تطبيق متساوي الحرارة لامتزاز Langmuir مع($R2 = 0.93$)

الخلاصة: تم تحضير البوليمر المستهدف وتأكيده بواسطة الأشعة تحت الحمراء، وهو مستقر حراريا بناء على تحليل TG وينتج عنه إزالة نسبة عالية من المعدن الثقيل.

الكلمات المفتاحية: كربوكسي ميثيل سلولوز، تلوث المياه، معالجة مياه الصرف الصحي، المعادن الثقيلة، النحاس، 2–أمينوبيريدين، ثنائي إيثيلين تريأمين.