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Faculty of Graduate Studies

**Anionic Microcrystalline Cellulose For Removal Pb⁺²
From Waste Water**

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the Degree of Master of Chemistry, Faculty of Graduate Studies,
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Anionic Microcrystalline Cellulose For Removal of Pb+2 From Waste Water Purification

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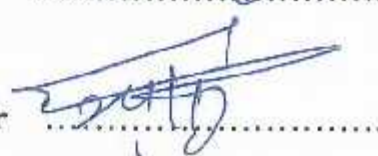
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Dedication

To my lovely parents, my family, thank you for your continuous support.

To my lovely husband, thank you from the bottom of my heart for your
greatest support. To my son who is all my life.

I thank God for being in my life. To my husband's family. To my
colleagues, and my friends.

To every teacher who taught me in my life, Thanks for your support that
reach me to what I am in it.

To my occupied country Palestine, our teaching is the weapon for us
against the Zionist occupation. Everyone who helped and supported me to
complete this research.

To all of them I dedicate this work.

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الافرار

أنا الموقعة أدناه، مقدّمة الرسالة التي تحمل العنوان:

Anionic Microcrystalline Cellulose For Removal Pb+2 From Waste Water

أقر بأن ما اشتملت عليه هذه الأطروحة إنما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد. وأن هذه الرسالة كاملة، أو أي جزء منها لم يقدم من قبل لنيل أي درجة أو لقب علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

Declaration

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

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List of Abbreviations

Symbol	Abbreviation
DNA	Deoxyribonucleic acid
EPA	Environmental Protection Agency
ΔE	Activation energy
OISW	Olive industry solid waste
BOD	Biological Oxygen Demand.
COD	Chemical oxygen demand
CMC	Carboxyl methylcellulose
CyDs	Cyclodextrins
β-CyD	Beta- Cyclodextrin
ICP-MS	Inductively Coupled Plasma Mass Spectrometry.
C_o	Initial metal ions concentration (mg/L)
C_e	Equilibrium metal ions concentration after subjecting it to treatment with adsorbent
CMC-CD-A	Carboxyl methylcellulose- Cyclodextrin-polymer A
CMC-CD- B	Carboxyl methylcellulose- Cyclodextrin-polymer B
CMC-CD- C	Carboxyl methylcellulose- Cyclodextrin-polymer C
AAS	Atomic Absorption Spectrophotometer
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
C_e	Equilibrium concentration of metal ion (ppm)
Q_e	Amount of adsorbate adsorbed per unit mass of cellulose amine at equilibrium (mg/g)
$Q_{\max}$	Theoretical maximum monolayer adsorption capacity of the adsorbent (mg/g)
K_L	Langmuir isotherm constant related to the adsorption energy (L/mg)
K_F	Empirical constants that indicate the relative adsorption capacity
$\frac{1}{n}$	Intensity related to the affinity of the metal
C_0	Initial adsorbate concentration
R_L	Dimensionless constant factor
Q_t	Adsorption capacities at equilibrium (mg/g)
t	Various times (min)
K_1	Pseudo-first-order rate constant (1/min)

K_2	Pseudo-second-order rate constant (g/mg min)
K_{id}	Intraparticle diffusion rate constant (mg/gmin ^{1/2})
Z	Thickness of the boundary layer
F	Fractional attainment of equilibrium (mg×g ⁻¹)
K_f	liquid film diffusion constant
ΔG_0	Gibbs free energy
ΔH_0	Enthalpy
ΔS_0	Entropy
K_c	Apparent constant of the thermodynamics
C_{ads}	Amount adsorbed at equilibrium (mg/L)
C_e	Equilibrium concentration in an aqueous solution of metal ion (mg/L)
R	The gas constant (J/mol × K)

**Anionic Microcrystalline Cellulose for Removal Pb⁺² From
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Abstract

The sources of safe drinking water on the planet are becoming exposed to contamination with toxic metals and organic matters. The reason was related to the spread of various industries and the development of life. These toxic materials present in water are dangerous can cause permanent damage to life on earth.

Current research in the area are focused on the development of methods for removing these toxic metals form water, as many chemical methods have been developed for water purification, purification methods that are simple and environment friendly are more attractive.

Cellulose is one of the most abundant natural polymers, and it has many advantages that make it an attractive candidate to be used in such purification processes, as its cheap, available, safe and biodegradable, which makes environmentally friendly polymer.

In the current research cellulose was used as a basic material in the formation of a 3D crosslinked polymer that was used in water purification from toxic metals. Cellulose was first convert to carboxymethylcellulose (CMC) by reacting cellulose with chloroacetate and sodium hydroxide

solution in isopropyl alcohol. The produced CMC was crosslinked with β -cyclodextrin at about 160 °C.

Three polymers of crosslinked cellulose and β -cyclodextrin (co- β -CMC-CD) A, B, and C were designed and synthesized. Various proportion of the materials were used for preparing the polymers. The polymers structures were analysed by FT-IR and the polymer morphologies were studied by (SEM). The adsorption efficiency of the three co- β -CMC-CD polymers toward Pb^{2+} from an aqueous solution was investigated as a function of adsorbent dose, temperature, pH and time, the adsorption parameters that lead to an excellent adsorption efficiency were determined. The polymer showed excellent efficiency toward Pb^{2+} . The highest adsorption efficiency was attained at pH 7.5, room temperature(20°C) for 30 min at 0.05 mg/L concentration. The high adsorption efficiency of the cellulose polymers could be attributed to the presence of various coordination sites which includes carboxyl, hydroxyl and β -cyclodextrin. Polymer B that contains equal quantities of β -cyclodextrin CMC showed little higher efficiency toward Pb^{2+} than the other two polymers. This could be due to the availability of both functionalities carboxyl groups and β -cyclodextrin. These results indicate that the inclusion and the complexation process are inclusion are equally important in the adsorption process.

The results indicate that, this work present and easy method for making an adsorbent with high efficiency .

Chapter One

Introduction

1.1 Background

Water contaminated with metal ions is a major worry due to their toxicity. The non-biodegradability of these metals and its high tendency to accumulate in living organisms [1-2] .make the situation ever worst. As this become a major concern, the issue of water contamination with heavy metal and the processes of removing them was given the status of high priority that requires immediate attention.

1.2 Heavy metals

Heavy metal ions with high toxicity and of a major concern are lead, mercury, chromium, arsenic, cadmium, nickel, selenium and zinc [3]. The presence of heavy metal in water sources is also a serious threat to the environment. Metals present in waste water are always in the migration state and tend to seep from waste, polluted soils into water stream. The metal ions concentrations tend to increase with time and as the level of food chain is passed onto a higher level in a phenomenon known as bio-magnification [2]. The high toxicity of these metals could cause severe damage to the human and other creatures even if they present at low concentrations. Their toxicities are related to their tendency to bind to protein in humans and other living creatures. This binding tends to stop the replication of DNA and thus prevent cell division [4]. So, it is important that water is purified from these toxic metal ions and removed from the

waste streams of industries and other contaminated water before its disposal. Some of the effect of these heavy metals are summarized below in Table 1.1[5].

Table 1.1: Heavy metal toxicity and the environment public health

Heavy metal	Major sources	Effect in human health	Allow level(mg/L)
Arsenic	Pesticides, fungicides, metal	Bronchitis, dermatitis	0.02
Cadmium	Welding, electroplating, pesticide	Kidney damage, bronchitis, cancer	0.06
Lead	Paint, pesticide, smoking	Liver, kidney, gastrointestinal damage	0.1
Manganese	Welding, fuel addition,	Contact causes damage to central nervous system	0.26
Mercury	Pesticides, batteries, paper industry	damage to central nervous system, protoplasm poisoning	0.01
Zinc	Refineries, metal plating, plumbing	Zinc fumes have corrosive effect on skin, causes damage to nervous membrane	15

The level according to the World Health Organization and US Environmental Protection Agency

One of the major sources of water contamination with metal ions is the industrial streams. That include mining, pesticides, pharmaceutical companies, plastics, rubber, and wood products. The heavy metals are carried by the wastewater downstream from the industrial sites.

The heavy metals present in water can either penetrate the cell or bind to the surface of microorganisms. If the metal penetrates the cell, this could cause a chemical changed to the cell structure of the organisms as they use chemical reactions to digest food [6].

For Instance, the main sources of copper in industrial effluents are metal cleaning and plating baths, pulp and paper industry, and fertilizer. Copper

is toxic to aquatic organisms even at very low small concentration. It is also used as micronutrient in agriculture, therefore, accumulate in surface waters. It is also essential to human life and health but, excessive intake of copper results in its accumulation in the liver and causes a gastrointestinal a problem [7].

1.2.1 Lead

Lead is a major concern of water pollution. The main sources of this toxic metal is combustion of automobile gasoline, battery manufacturing, electroplating industry, printing and painting processes and plumbing [8]

Lead in nature is a bluish-grey present in small amounts in the earth's crust metals with an atomic weight and atomic number of 207.19 and 82, respectively [9].

It is widely used in industry and as mentioned before lead is toxic and nonbiodegradable it stays in the environment for long period of time. The concentration of lead in drinking water should not exceed 0.1 mg/L [10].

Lead compounds like most transition metal compounds counted as cumulative poisons [11]. Lead has a significant role in many industries because it is ductile and easily shaped. It has been used in many sectors and products: batteries, petrol additives, chemical compounds, pigments, and cables. Accordingly, lead can find a pathway to human beings through drinking water, food, air, soil and dust. They enter the environment through mainly for industry discharges [11,12]. Lead concentrations in wastewater

from battery manufacturing, acid mine drainage, tailing pond and steel production plants range from 0.5 to 25 mg/L [13].

Lead pollution is considered one of the most serious environmental problems and causes several serious health issues. Exposure to lead could occur through inhalation of lead dust particles or aerosols and ingestion of lead-contaminated food, paints and water contaminated with lead due to corrosion of piping used in water distribution system [12,14]. Among the health issues caused by lead are for instance, in the human body, it attacks the nervous system and causes damage to the reproductive system, liver, kidney, basic cellular processes, brain functions [15] and abnormalities in infants [11,16]. Overdoses of lead and long-term exposure can cause severe impacts especially on infants. According to the Environmental Protection Agency (EPA) high concentrations of lead may cause acute or chronic damage to the nervous system and problems in the synthesis of haemoglobin , effects on the kidney, gastrointestinal tract, joints and reproductive system. It also tends to decreased growth, hyperactivity, impaired hearing, brain damage and mental and psychological developments in infants as shown by several studies.

1.3 Treatment methods for heavy metals in wastewater

A large number of techniques for the removal of heavy metals from wastewater are available. Among these are ion exchange, chemical precipitation, electrolytic recovery, adsorption, electro dialysis, reverse osmosis, solvent extraction, membrane separation, ozonation, freeze

crystallization, ultrafiltration foam floatation, and photochemical methods. Some of these treatment methods could be successfully used for wastewater purification, others could be limited in use. For instance, the chemical precipitation is not useful for use with the solutions of low concentration [13]. Adsorption by ion exchange and activated carbon are quite expensive and require recharge of resin and activated carbon, in addition, the disposal of large volume of solution. The membrane technology is also too expensive and the membranes are susceptible to attack by germs. Other methods mentioned above require high operation costs.

In general, method used for wastewater purification from heavy should have high rate of removal, low cost in terms of labour and materials, regeneration, metal recovery, equipment and energy, applicable in small to large scales, generate low volume of highly enriched spent materials and capability of removing heavy metal ion to a level below established regulatory standards [16].

Adsorption process could be the most appropriate in regard to its effectiveness, economic and easily available adsorbents which makes it a promising process by meeting the criteria mentioned above [17,18].

1.3.1 Adsorption Method

Adsorption was discovered in the 1700's for gases, Lowitz used adsorption method in the late 1700's for other media [19]. Now adsorption is a

becoming a versatile and significant in various applications. Adsorption on solids is mainly used for water and wastewater purification, mainly using activated carbon. Other useful absorbents are silica gel, treated acid clay, agricultural wastes and metal oxides [20]. For instance, Smith in 1998 developed method of using recycled iron to remove metals from aqueous solutions. The adsorption process was conducted using fixed bed and batch reactor systems. The uptake capacity of the iron adsorbent was favourable when compared to commercial adsorbents.

The main attribute of a good adsorbent is a large surface area (highly porous). The larger the surface area, the more molecules are bonded to the surface. The specific surface area is the surface area available for adsorption per gram of the adsorbent. It is also could be affected by factors such as pH, temperature, time and concentration of adsorbents and adsorbates [21,22]. So, adsorption could mean the process of build-up of any substance giving higher concentration of molecular species on the surface of an adsorbent as compared to that in the solution. Adsorption is a well-known and powerful technique for cleaning industrial effluents as well as domestic effluents [23].

1.3.2 Types of Adsorption Forces

The type of adsorption could be divided into two types based on the type of forces created between adsorbent and adsorbate. The forces could be physical or chemical.

1.3.2.1. Physical Adsorption

When the attraction forces existing between adsorbate and adsorbent are Vander Waal or H-bonding, the process is called Physical Adsorption (Physisorption). Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent [22,24]. It takes place at low temperature. As the temperature rise up Physical adsorption decreases. It is an exothermic process with low enthalpy values (20–40 kJ mol⁻¹). The activation energy (ΔE) is low so it could be a reversible process.

The physical adsorption occurs more readily at lower temperatures and decreases by increasing the temperature.

1.3.2.2 Chemical Adsorption or Chemisorption

When the attraction forces between adsorbate and adsorbent are chemical, the process is called Chemical Adsorption (Chemisorption). It occurs with the formation of unilayer of adsorbate on adsorbent. The enthalpy of adsorption is high (80-240 kJ mol⁻¹) [24]. It increases as the temperature increases Chemisorption is highly specific and occurs only in case of chemical bonding between adsorbent and adsorbate.

Polymeric based adsorbents constitute a new and novel class of adsorbents, they showed large specific surface areas and highly [25]. These characteristic makes these polymers effectively adsorb metals from aqueous solutions. In this work cellulose with ionic functionality will be synthesized and used in extraction of metals ions such as lead from an

aqueous solution. In order to reduce its solubility in water it will be cross linked with polar natural product such as cyclodextrin .

1.4 Cellulose

Cellulose chosen for the present work will be extracted from the olive industry solid waste (OISW) using a process developed at our laboratories. In general, olive mill waste consists of about 44% of olive industry solid wastes (OISW) and 56% of olive industry liquid waste (OILW) [26]. These wastes are acidic, have extremely high biological oxygen demand (BOD) and chemical oxygen demand (COD) values, and also contain high toxic levels of polyphenols [27]. The waste materials pose a challenge in waste management to the olive mills and a concern to environmentalists, for it presents a serious disposal problem. In addition to this, olive industry loses economic value by disposing the effluent or selling it for a low price to other industries. In certain countries, the OISW is usually burned or left to rot, thus releasing CO₂ into the atmosphere, while OILW tends to be disposed of via the sewage system, which has implications for water quality. So, olive industry waste is a major problem faced by industrialist in view of increasing environmental standards day by day. In addition to this, olive industry loses economic value by disposing the effluent or selling it for a low price. The challenge is to utilize and convert these waste materials into useful and low-cost marketable products.

Cellulose is a linear polymer made of the monomer D-glucose that are linked successively through β -1,4-glycosidic bonds in the β -configuration between carbon 1 and carbon 4 of adjacent units to form a Polymeric chain

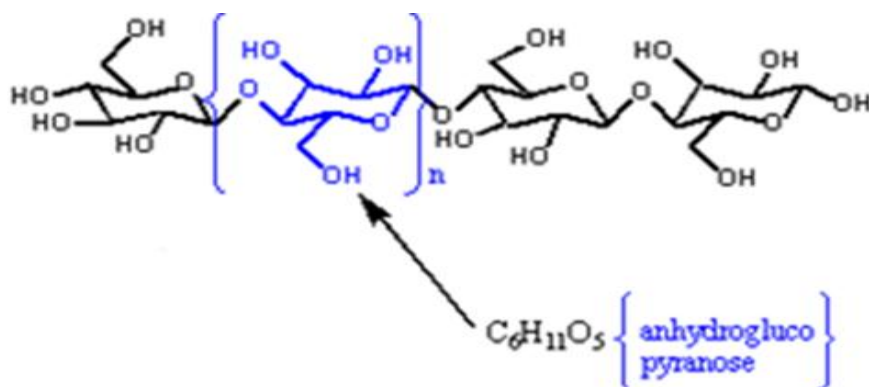


Fig 1.1: Cellulose chemical structure.

Each D-anhydroglucopyranose unit possesses hydroxyl groups at C2, C3, and C6 positions, capable of undergoing the typical reactions known for primary and secondary alcohols.

Cellulose has been industrial feedstock for a large number of derivatives with unlimited number of commercial applications, and also an important source for ethanol when chemically or enzymatically hydrolyzed into glucose [30]. Surface modified cellulose also of great interest due to a wide range of potential applications [28].

Cellulose is the natural polymer that was evaluated most in this area of research [29-10]. In one study, a chemically modified cellulose bearing pendent methyl benzaniline chelating group was synthesized. The modified cellulose was used for the removal of Cu^{+2} and Pb^{+2} from aqueous

solution. The adsorption kinetic parameters fitted well to the pseudo-second-order kinetic model [12].

In another study microspheres of cellulose and polyethylene mine were prepared then cross-linked by glutaraldehyde. The cellulose microspheres were used to study Pb^{+2} removal efficiency from aqueous solution on the basis of adsorption kinetics and isotherm equations. The results showed that adsorption capacity on Pb^{+2} of modified cellulose microspheres was 9.46 mg/g which is higher by about 50% compared with the adsorption capacity of cellulose microspheres. In addition, it was found that, the adsorption process fit pseudo second order kinetics equation and Freundlich isotherm equation [9].

Celluloses ester was also used for this purpose, it was prepared by reacting cellulose derived from cheap filter paper was reacted with succinic anhydride in solid state. The prepared cellulose ester was evaluated in extraction of Cu^{+2} from waste water. The Cu^{+2} removal by the cellulose ester reached 94% at $\text{pH} = 4.0\text{-}5.0$ after reaction for 50 min at room temperature [30] . In an invention, an amino-modified sawdust adsorbent was also used in purification of waste water [31].

Cellulose modified with thiosemicarbazide group was evaluated as adsorbent for Hg^{+2} from water, the results demonstrated that the thiosemicarbazide modified cellulose possessed high performance for Hg^{+2} adsorption from water with a adsorption capacity of 499.6 mg/g . The sorption model followed Langmuir model and pseudo-second order kinetic

model. The fitting coefficient (R^2) was more than 0.98. The enhanced Hg^{+2} adsorption capability of thiosemicarbazide modified cellulose was related to chelating interaction between Hg^{+2} and thiosemicarbazide [32].

In this work the synthesis and characterization of a novel anionic cellulose possesses with high affinity toward toxic metals will be synthesized. The ionic cellulose chosen for this work is carboxymethylcellulose (CMC).

1.4.1 Carboxymethylcellulose (CMC)

Carboxymethylcellulose is a water-soluble cellulose ether with carboxyl and hydroxyl groups, it shows pH sensitivity. CMC a biodegradable, non-toxic, biocompatible and cheap ionic polysaccharide that [33-34].

Carboxymethylation showed a wide range of promising properties. Usually prepared by Williamson ether synthesis from activated cellulose with monochloroacetic acid or its sodium salt [35].

It has unlimited number of applications such as controlled drug releases Cyclodextrins (CyDs) are cyclic oligosaccharide composed of 6 to 8 glucopyranose units (namely α -, β - and γ -CyDs) linked by glycosidic bonds. All are water soluble, non-toxic and hydrophilic at the surface and hydrophobic in the central cavity [30]. The large number of the hydroxyl groups in cyclodextrins are considered binding sites and able to form analyse types of linkages. A cross-linking with other compounds or polymers, or they derivatization are considers the main reactions of these cyclodextrins. Moreover, they are able to form complexes with polymers

and various substrates, thus changing their physicochemical properties [31].

β -CyD is available at low cost. It has been widely used in adsorption, as a catalyst and in organic synthesis. β -CyD showed excellent activity as a catalyst in liquid oxidation, however the isolation of β -CyD from a homogeneous system is not simple and costly. For this reason, β -CyD was fixed on supports, such as for instance polymeric and mineral materials. This way the catalytic cycles was enhanced and the separation became simple [30].

In this work, it was converted to insoluble in water and used in waste water purification. The crosslinking will be carried out by reacting it with polycarboxylic acid compounds such as citric acid. The cross-linking will be carried out at elevated temperature (160C°). At this temperature, it for anhydride by a condensation process then crosslink with β -cyclodextrin. The cross-linking adds a new functionality to β -cyclodextrin that is carboxyl groups. These properties make β -cyclodextrin excellent candidate for application in waste water purification from both metals and organic materials.

1.4.2 β -Cyclodextrins

β -cyclodextrin usually produced by enzymatic hydrolysis of starch, the enzymatic process was discovered in 1891. The industrial applications of β -cyclodextrin became valuable in 1970s, and currently thousands of tons of

β -cyclodextrin and is produced annually [32]. The structure of β -cyclodextrin consist of seven glucopyranose units as shown in Figure 1.2, [29].

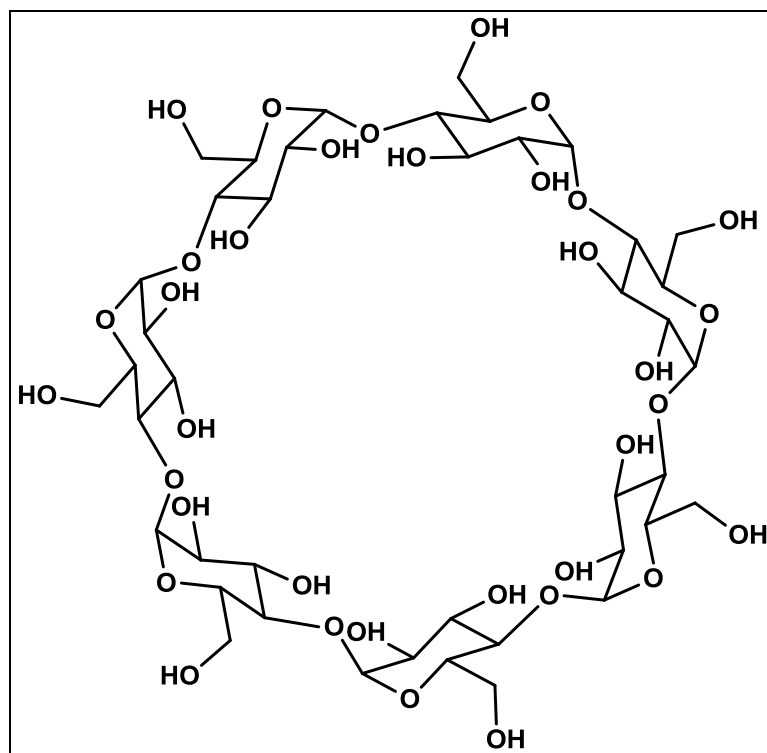


Figure 1.2: The chemical structure of β -cyclodextrin.

Cyclodextrin has a cone-shaped with secondary and primary hydroxyl groups, where the secondary groups extend from the widest edge and the primary one extends from the narrow edge as shown in following figure 1.3 [26].

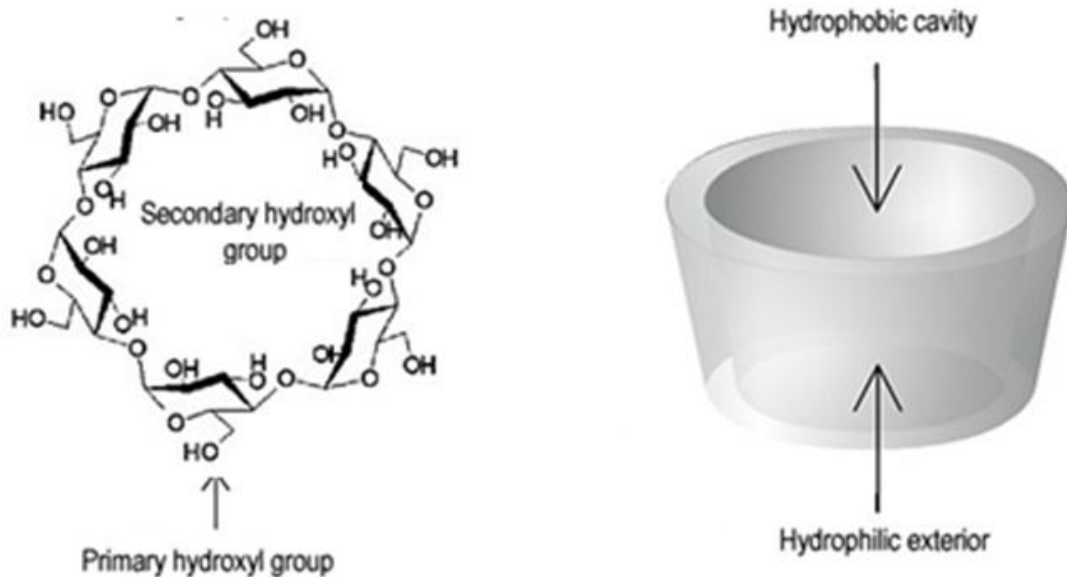


Figure 1.3: A diagram of a β -cyclodextrin showing the arrangement of a glucose unit and the conical structure [27].

Regarding the solubility of β -cyclodextrins, it is more soluble in water but has poor in organic solvents.

1.4.2.1 Applications of β -Cyclodextrin

B-Cyclodextrins has a wide range of applications, which was attributed to its ability for complexation and other versatile characteristics. One of its main application is in pharmaceutical products [14]. The cavity diameter of β -cyclodextrin was found to be an appropriate size for vitamins, hormones, and other compounds specially those used in cell culture applications and tissue.

β -Cyclodextrins and its derivatives have been widely used as a dispersion vehicle in systems such as emulsions, microspheres, nanospheres, microcapsules, nanocapsules, and niosomes. Cyclodextrin is also used to increase drug loading of polymeric microspheres [14]. A series of CD derivatives are also widely known in the food, cosmetic and toiletries and biotechnology and pharmaceutical industries [32].

In this work CMC was prepared then crosslinked to enhance its metal adsorption properties and reduce its water insolubility.

1.5 Scope of this work

1. To synthesize anionic microcrystalline cellulose and use it as a binder form metals present in wastewater and other contaminated sources.
2. Converting cellulose to ionic cellulose by reacting it with sodium chloroacetate.
3. Crosslinking the anionic cellulose with β -cyclodextrin.
4. Evaluate the possibility of using the prepared the crosslinked anionic microcrystalline cellulose in waste water purification.
6. Characterize the new polymers by various spectroscopic techniques.

Chapter Two

Experimental

2.1 General experimental

All reagents used in this study were purchased from Sigma-Aldrich (located in Jerusalem) and used as received without any further purification.

2.1.1 Instrumentation

The following instruments were used to accomplish the present research: Water bath equipped with a thermostat and a shaker with a digital Speed control and with condenser connected to nitrogen gas, a pH meter, FT-IR Spectrometer and FAAS.

The functional groups of the produced polymers were checked by Fourier transform infrared spectrometer (FT-IR), which were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) and equipped with the Smart Split Beam Hemi Micro ATR accessory (International Crystal Laboratories, Garfield, NJ, USA). The following parameters were used: resolution was 4 cm^{-1} , spectral range was 600 cm^{-1} to 4000 cm^{-1} and number of scans was 128.

The Pb^{+2} solution concentrations studied used in this work were measured determined by Flame Atomic Absorption Spectrometer at wavelength of 217 nm (ICE 3xxx C113500021 v1.30) to determine residual Lead ions

concentration. The error range in the experimental data were analysed using Microsoft Excel, a certainty interval of 95% was used.

2.1.2 Materials

Reagent solvents and chemicals used in this work were of analytical grade and used as received. They were purchased from the local market. The reagents were isopropyl alcohol, sodium hydroxide, sodium chloroacetate, acetic acid, methanol, lead nitrate and β -cyclodextrin.

All solutions were prepared using deionized water.

2.2 Convert cellulose to carboxymethylcellulose (CMC)

A sample of microcrystalline cellulose (10.0 g OD weight, 0.062 mol of anhydroglucose repeat unit) was charged into a 1 L Pyrex reaction kettle. The reaction kettle (1.0 L) was outfitted as follows: with a thermocouple inserted through a rubber septum, a Teflon bladed agitator on a glass shaft attached to a mechanical mixer, a gas inlet Nitrogen tubing inserted through an adapter fitted with a rubber septum, and a gas outlet adapter connected to a gas trap partially filled with oil. To the pulp in the kettle was added isopropyl alcohol (150 mL) and water (15 mL). The mixture in the reaction kettle was agitated and purged with nitrogen gas for about 10 minutes. Sodium hydroxide solution (50%, 9.0 g, 0.103 mol) was added to the mixture dropwise over a period of 5 min, followed with a second addition of isopropyl alcohol (40 mL). A suspension of sodium chloroacetate (16.0 g, 0.13 mol) in a mixture of isopropyl alcohol (30 mL)

and water (5 mL) was added to the reaction mixture in one portion. The produced mixture was stirred and heated to 60 °C over a period of 1 hr then maintained at 60 °C for another 1 hr. The reaction was quenched by the addition of acetic acid (26.0 g), collected by suction filtration, washed three times with a solution of methanol (100 mL) and water (50 mL) then with neat methanol alone and dried at 60 °C. A quantitative yield was obtained.

2.3 Synthesis Cross-linking of carboxymethylcellulose (CMC) with β -cyclodextrin (β -CD)

Three crosslinked polymers were prepared with various rations of CMC and β -CD. The detailed procedure is shown below.

2.3.1 Synthesis of carboxymethylcellulose (CMC) with β -cyclodextrin (β -CD) Polymer CMC-CD-A

A solution of CMC and β -cyclodextrin in a 1:3 ratio (0.5 g and 1.5 g, respectively) was prepared in deionized water (20.0 mL). The solution was stirred until became clear. The solution was placed in an oven at 110 °C to evaporate the water. Then, the oven temperature was raised to about 160 °C, and the solution was kept at this temperature for 30 min. The produced crosslinked polymer was removed from oven, cooled down to room temperature and ground then analysed by FT-IR spectroscopy.

2.3.2 Synthesis of carboxymethylcellulose (CMC) with β -cyclodextrin (β -CD) Polymer CMC-CD-B

A solution of CMC and β -cyclodextrin in a 1:1 ratio (1.0 g each) was prepared in deionized water (20.0 mL). The solution was stirred until became clear. The solution was placed in an oven at 110 °C to evaporate the water. Then, the oven temperature was raised to about 160 °C, and the solution was kept at this temperature for 30 min. The produced crosslinked polymer was removed from oven, cooled down to room temperature and ground then analysed by FT-IR spectroscopy.

2.3.3 Synthesis of carboxymethylcellulose (CMC) with β -cyclodextrin (β -CD) Polymer CMC-CD-C

A solution of CMC and β -cyclodextrin in 3:1 ratio (1.5 g and 0.5 g, respectively) was prepared in deionized water (20.0 mL). The solution was stirred until became clear. The solution was placed in an oven at 110 °C to evaporate the water. Then, the oven temperature was raised to about 160 °C, and the solution was kept at this temperature for 30 min. The produced crosslinked polymer was removed from oven, cooled down to room temperature and ground then analysed by FT-IR spectroscopy.

2.4 Solubility of crosslinked polymer in water

A 1.0 g small sample of each of the synthesized polymers was suspended in a 50.0 mL water and stirred for 1 hr at room temperature. The polymer was

then collected by filtration and dried at 110 °C a constant weight was obtained.

2.5 Lead metal ion adsorption from contaminated water

2.5.1 Preparation of lead solutions

A stock solution of Pb^{+2} with a (100.0 mg/L) concentration was prepared by dissolving (0.16 g) of lead nitrate in a 100.0 mL distilled water and used as a stock solution.

Then various solutions with concentrations of 1.0 ,5.0, 10.0, 20.0, and 50.0 mg/L were prepared from the stock solution by dilution using the relationship ($C_1V_1 = C_2V_2$).

2.5.2 Calibration curve

Calibration curve was prepared and used to determine the concentration of Pb^{+2} in solution after treatment with adsorbents.

The absorbance of solutions of Pb^{+2} with known concentrations were determined by Atomic Absorption Spectrophotometer (AAS) and the results were used to construct the a calibration curves. According to Beer-Lambert law, the absorbance and concentration are directly proportional. By applying the Beers .This law can be used to an determine an unknown concentration can be determined. The constructed calibration curve are shown in Figure 2.1:

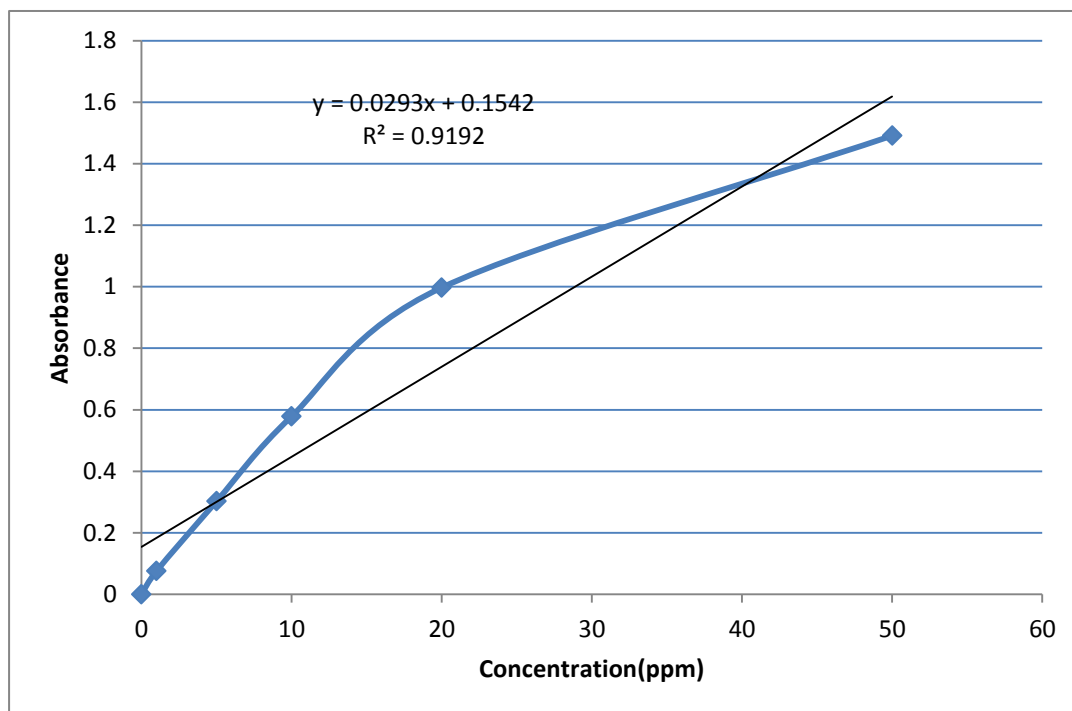


Figure 2.1: Calibration curve of Pb(II).

2.5.3 Lead(II) adsorption

A batch extraction process was adapted in this work. In this process a known amount of crosslinked polymer adsorbent was added to lead metal ion solution with known concentration in a container, then the container is closed and stirred under certain conditions. Then a small sample of the

mixture is withdrawn with a syringe, filtered through a (0.45 μm) syringe filter and analysed to determine the amount of metal ion not adsorbed by atomic absorption spectroscopy.

The percentage of metal ion (% Adsorption) adsorbed is calculated as shown in the following equation (Eq. 2.1). In the equation the amount of residual metal ions is subtracted from the initial concentration of the metal ions and divided by the initial concentration of Pb^{+2} [36].

$$\text{Removal efficiency (\%)} = \left[\frac{(C_o - C_e)}{C_o} \right] \times 100 \quad (2.1)$$

C_o is the Initial metal ions concentration (mg/L) and C_e is the equilibrium (residual) metal ions concentration after subjecting it to treatment with adsorbent.

2.5.3.1: The effect of polymer dose on lead removal efficiency

The adsorption efficiency of the adsorbents (**CMC-CD-A**, **B** and **C**) was evaluated as a function of adsorbent dose at constant pH, time, temperature and initial Pb^{+2} concentration. Five solutions each 10.0 mL and a concentration of 20.0 mg/L were prepared in five plastic containers each treated with different amount of adsorbent (0.005 g, 0.025 g, 0.05 g, 0.1 g, 0.2 g) at pH 7.5.

The solutions were stirred for 30 min, at room temperature. A sample of each solution was collected using a syringe, filtered through a 0.45 μm syringe filter and analysed for residual Pb^{+2} concentrations by AAS.

The collected results for three polymers are summarized in the following tables:

Table 2.1: Effect of polymer dose on lead removal efficiency of adsorbent CMC-CD-A.

Adsorbent dose (mg)	Pb ²⁺ Removed (%)
0.005	57.4
0.025	68.6
0.05	78.3
0.1	79.4
0.2	82.3

Table 2.2: Effect of polymer dose on lead removal efficiency of adsorbent CMC-CD-B.

Adsorbent dose (mg)	Pb ²⁺ Removed (%)
0.005	61.4
0.025	71.4
0.05	88.6
0.1	88.7
0.2	90.1

Table 2.3: Effect of polymer dose on lead removal efficiency of adsorbent CMC-CD-C.

Adsorbent dose (mg)	Pb ²⁺ Removed (%)
0.005	67.2
0.025	69.3
0.05	81.7
0.1	80.9
0.2	81.9

2.5.3.2: The effect of lead nitrate concentration on lead removal efficiency

The adsorption efficiency of the adsorbents (CMC-CD-A, B and C) was evaluated as a function of initial Pb⁺² concentration at constant pH, time,

temperature and adsorbent dose. Five solutions of lead nitrate with various concentrations (1, 5, 10, 20 and 50 mg/L) were prepared from the stock solution (100.0 mg/L). Three sets of solutions were prepared, the pH was set at 7.5 and at room temperature. Then treated with fixed weight of adsorbents (0.05 g of each polymers **CMC-CD-A, B** and **C**) . The solutions were stirred for 30 min, (For each 0.05 g, 30 minutes shaking at room temperature. A sample of each solution was collected using a syringe, filtered through a 0.45 μm syringe filter and analysed for residual Pb^{+2} concentrations by AAS.

The obtained results are summarized in the following tables:

Table 2.4: The effect of Lead nitrate concentration on lead removal efficiency for Adsorbent CMC-CD-A.

Lead nitrate Concentration (ppm)	Pb^{2+} Removed (%)
1	98.7
5	97.2
10	96.5
20	93.2
50	78.6

Table 2.5: The effect of Lead nitrate conc. on lead removal efficiency of adsorbent CMC-CD-B.

Lead nitrate Concentration (ppm)	Pb^{2+} Removed (%)
1	99.2
5	98.4
10	95.3
20	94.1
50	68.4

Table 2.6: The effect of Lead nitrate conc. on lead removal efficiency of adsorbent CMC-CD-C.

Lead nitrate Concentration (ppm)	Pb ²⁺ Removed (%)
1	96.7
5	94.3
10	93.8
20	92.1
50	57.2

2.5.3.3: The Effect of temperature on lead removal efficiency

The adsorption efficiency of the adsorbents (CMC-CD-A, B and C) was evaluated as a function of temperature at constant adsorbent dose, pH value, contact time and initial Pb⁺² concentration.

Five solutions each 10 mL with concentration of 20 mg/L and a pH value of 7.5 were prepared in five plastic containers, each treated with 0.05 g adsorbent.

The solutions were stirred for 30 min at various temperatures. A sample of each solution was collected using a syringe, filtered through a 0.45 µm syringe filter and analysed for residual lead ions concentrations by AAS.

The collected results for three polymers are summarized in the following tables:

Table 2.7: Effect of temperature on lead removal efficiency of adsorbent CMC-CD-A.

Temperature (°C)	Pb ²⁺ removal (%)
20	44.5
25	46.2
30	48.1
40	50.2
50	46.1

Table 2.8: Effect of temperature on lead removal efficiency of adsorbent CMC-CD-B.

Temperature (°C)	Pb ²⁺ removal (%)
20	47.2
25	46.3
30	45.2
40	44.9
50	40.5

Table 2.9: Effect of temperature on lead removal efficiency of adsorbent CMC-CD-C.

Temperature (°c)	Pb ²⁺ removal (%)
20	57.0
25	52.3
30	42.1
40	38.0
50	33.6

2.5.3.4: The effect of pH value on lead removal efficiency

The adsorption efficiency of the adsorbents (CMC-CD-A, B and C) was evaluated as a function of pH value at constant adsorbent dose, temperature, contact time and initial Pb⁺² concentrations. Five solutions each 10 mL with concentration of 20 mg/L and various pH values were prepared in five plastic containers, each treated with 0.05 g adsorbent at room temperature.

A sample of each solution was collected using a syringe, filtered through a 0.45 μm syringe filter and analysed for residual Pb^{+2} concentrations by AAS

The collected results for three polymers are summarized in the following tables:

Table 2.10: Effect of pH value on lead removal efficiency of adsorbent CMC-CD-A.

pH Value	Pb^{2+} Removed (%)
5	77.9
6.5	84.8
7.5	94.6
9	89.1
11	88.3

Table 2.11: Effect of pH value on lead removal efficiency of adsorbent CMC-CD-B.

pH	Pb^{2+} Removed (%)
5	85.1
6.5	86.8
7.5	90.1
9	87.3
11	86.1

Table 2.12: Effect of pH value on lead removal efficiency of adsorbent CMC-CD-C.

pH	Pb^{2+} Removed (%)
5	84.2
6.5	86.1
7.5	88.9
9	87.2
11	84.6

2.5.3.5: The effect of Contact Time on lead removal efficiency

The adsorption efficiency of the adsorbents (CMC-CD-A, B and C) was evaluated as a function of contact time at constant pH, adsorbent dose, temperature and initial Pb^{+2} concentration.

Five solutions each 10 mL and concentration of 20 mg/L were prepared in five plastic containers, each treated with 0.1 g adsorbent at pH 7.5.

The solutions were stirred for various period of time at room temperature. A sample of each solution was collected using a syringe, filtered through a 0.45 μm syringe filter and analysed for residual lead ions concentrations by AAS

The collected results for three polymers are summarized in the following tables:

Table 2.13: Effect of contact time on lead removal efficiency of adsorbent CMC-CD-A.

Adsorption time (min)	Pb^{2+} Removed (%)
1	37.4
5	67.1
15	77.3
30	79.4
60	79.5

Table 2.14: Effect of contact time on lead removal efficiency of adsorbent CMC-CD-B.

Adsorption time (min)	Pb ²⁺ Removed (%)
1	41.4
5	64.1
15	86.5
30	88.7
60	90.1

Table 2.15: Effect of contact time on lead removal efficiency of adsorbent CMC-CD-C.

Adsorption time (min)	Pb ²⁺ Removed (%)
1	37.4
5	59.5
15	80.1
30	80.9
60	81.9

2.6 Kinetics of adsorption process

The adsorption of Pb⁺² using the crosslinked polymer **CMC-CD-A** was subjected to kinetic study. The study was carried out using the optimized adsorption condition of polymer dose, pH value, contact time, concentration of metal ions, and temperature. The concentration of Pb⁺² was determined before and after treatment with the **CMC-CD-A**. The collect data were to analysis by Langmuir and Freundlich adsorption isotherm equations.

Amount of 0.05 g of **CMC-CD-A** was added to 10.0 mL of 20.0 mg/L of lead ions solution at pH of 7.5 . The mixture was placed at 20°C and mixed for 30 min . The rate of adsorption was followed during this period of time

and coordinated to theoretical models. Pseudo first-order and second-order kinetic models were tested in this study using collected data. Parameters such as K , Q_e and R^2 for Pb^{+2} adsorption by **CMC-CD-A** were determined, then compared with the theoretical values.

2.7 Metal ions adsorption from wastewater

A sample of sewage water was collected from a sewer system (Palestine) and used in this study. Qualitative and quantitative analysis was carried out on the sample by using ICP-AES (Water Center at An-Najah National University, Nablus, Palestine). Three samples of sewage each 10.0 mL were placed in three plastic containers and their pH values were adjusted 7.5. The three samples were labeled as 1, 2, and 3 and treated with 0.05 g of **CMC-CD-A**, **CMC-CD-B** and **CMC-CD-C**, respectively. The mixtures were shaken at room temperature for 30 min. A 5.0 mL sample of each mixture was withdrawn with a syringe and filtered through a 0.45 μm syringe filter and subjected to analysis by ICP-AES.

Chapter Three

Results and Discussion

3.1 Preparation of the crosslinked polymer carboxymethylcellulose / β -cyclodextrin

Carboxymethylcellulose was prepared as shown in Figures 3.1 and 3.2. The preparation was carried out by reacting cellulose extracted from olive industry solid waste (37). with sodium hydroxide in isopropyl alcohol then with sodium chloroacetate.

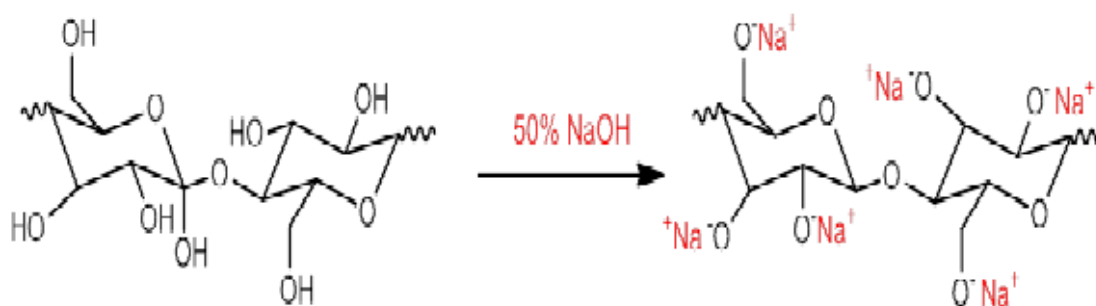


Figure 3.1: Ccnversion of Cellulose into by Treatment eith Sodium Hydroxide.

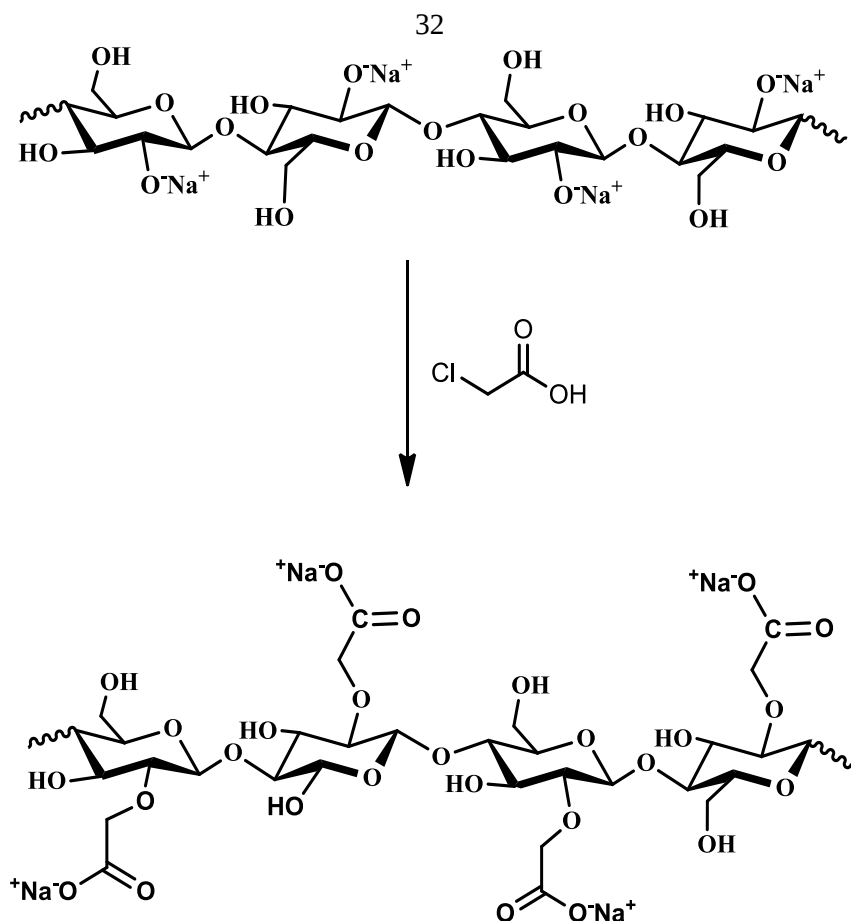


Fig. 3.2: Conversion of cellulose alkoxide into CMC.

The prepared CMC, then was crosslinked with β -cyclodextrin. A solution of CMC and β -cyclodextrin was prepared in water, which then evaporated to dryness at non curing temperature ($110\text{ }^\circ\text{C}$). A solution of the two materials was prepared in order to obtain a homogeneous mixture, where the molecules of the two chemicals are distributed evenly. The curing process (crosslinking) was promoted by heating the mixture at $160\text{ }^\circ\text{C}$ for at least 30 min. As shown in Fig 3.3 at $160\text{ }^\circ\text{C}$ the nearby carboxyl groups in CMC undergo condensation reaction and loses a water molecule to form anhydride. The anhydride is very reactive intermediate, it undergoes nucleophilic addition reaction with hydroxyl group of the β -cyclodextrin as

shown in Figure (3.4) to form an ester functionality as a linkage between the two materials.

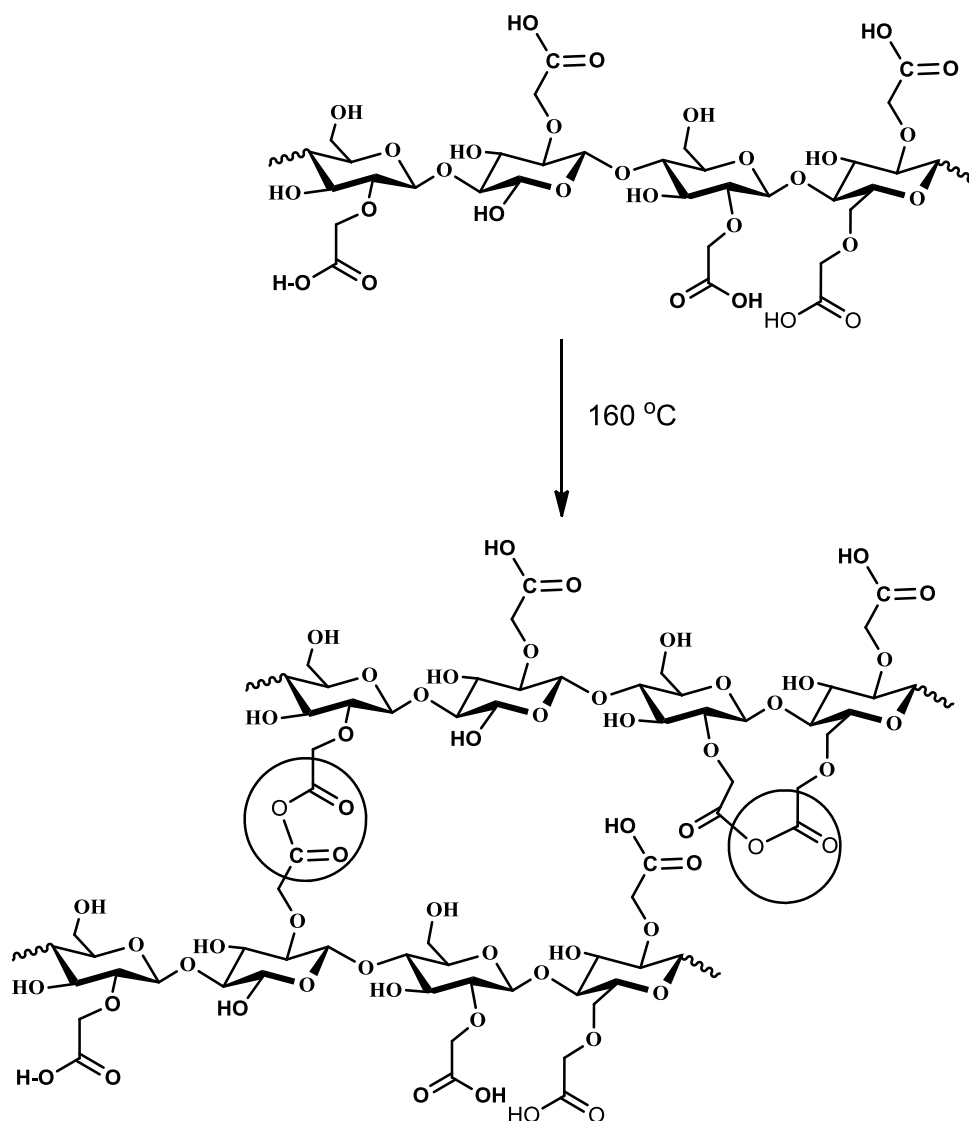


Figure 3.3: formation of anhydride from CMC.

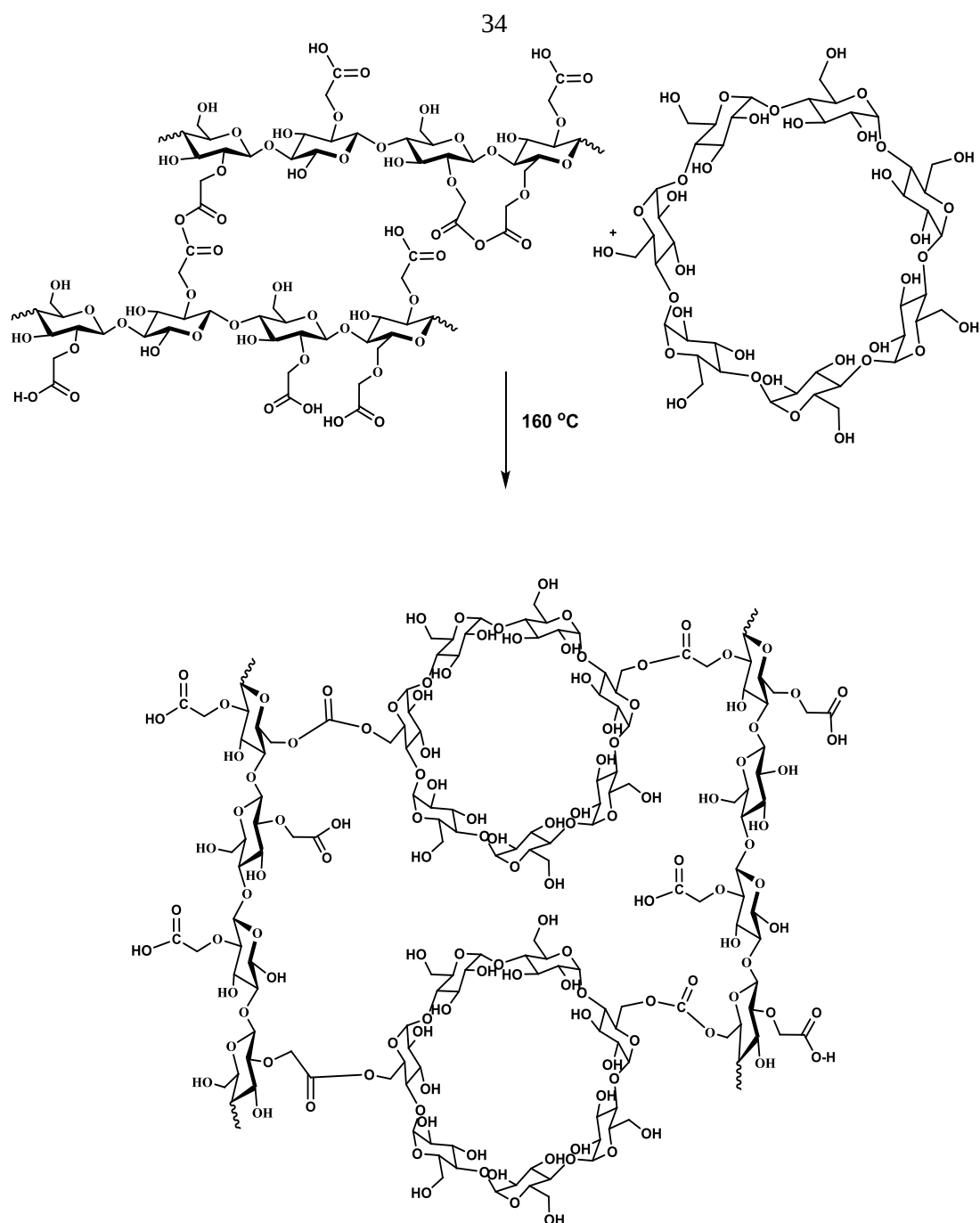


Figure 3.4: formation of CMC-CD.

A representative 3D structure of the produced co- β -CMC-CD is shown in figure 3.5. the figure shows all metal chelating sites

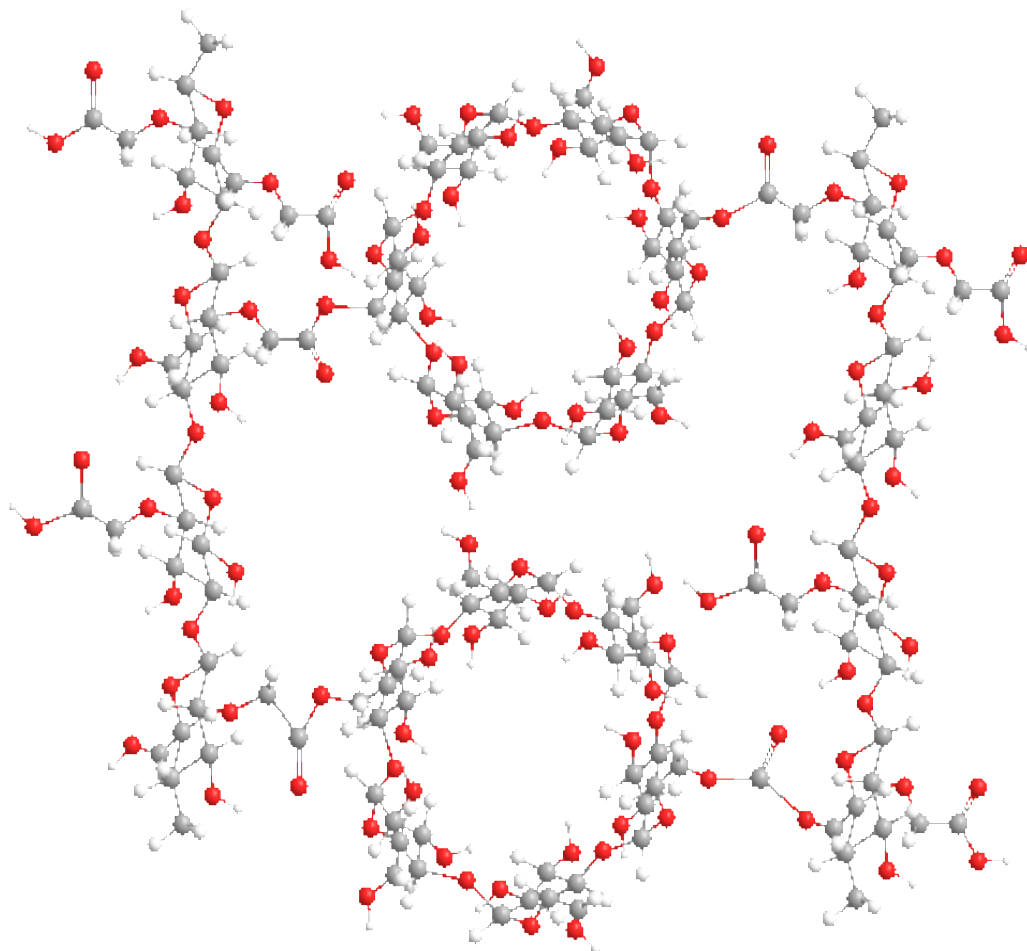


Figure 3.5: A 3D structure of CMC-CD.

3.2.FT-IR Characterization of the prepared CMC-CD polymers

The products formed from the reaction between CMC and β -cyclodextrin polymers (CMC-CD-A, B and C) were evaluated using FT-IR. The FT-IR spectrum of the starting materials CMC is shown in Figure 3.6. As shown in Figure 3.6, the FT-IR spectrum of CMC shows two sharp peaks at about 1705 and 1646 cm^{-1} which are crossbonding to the C=O of carboxylate and carboxyl groups, the peak at 1599 is a characteristic of cellulose.

The peak cross bonding to C=O showed as strong broad in (CMC-CD-A) polymer at about 1653 cm^{-1} , The peak shape could be an indication of the formation a new carbonyl group beside the acid carbonyl, that is as an ester group. The 1069 peak intensity dropped in polymer A, since amount of CD is the lowest in polymer A. The FT-IR also show the presence of C–H stretching vibration absorption bands at 2836 cm^{-1} for polymer A , 2945 cm^{-1} for polymer B and 2947 cm^{-1} for polymer C. Also, FT-IR showed the presence of the broad absorption band at 3285 cm^{-1} for O-H of carboxyl, and alcohol. The stretching frequency of O-H appear at 3397 cm^{-1} for polymer A , 3329 cm^{-1} for polymer B, and at 3357 cm^{-1} for polymer C, assigned to O–H stretching. These evidences confirm the formation of an ester linkage between β -cyclodextrin and CMC [38,39].

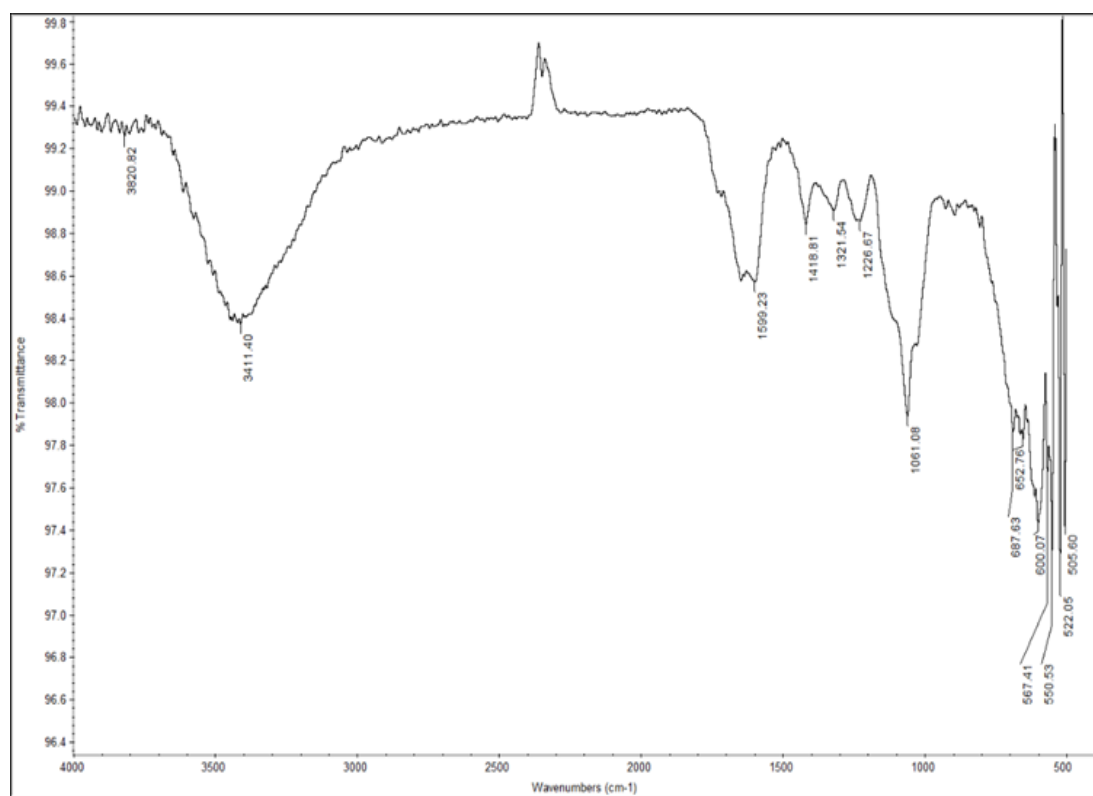
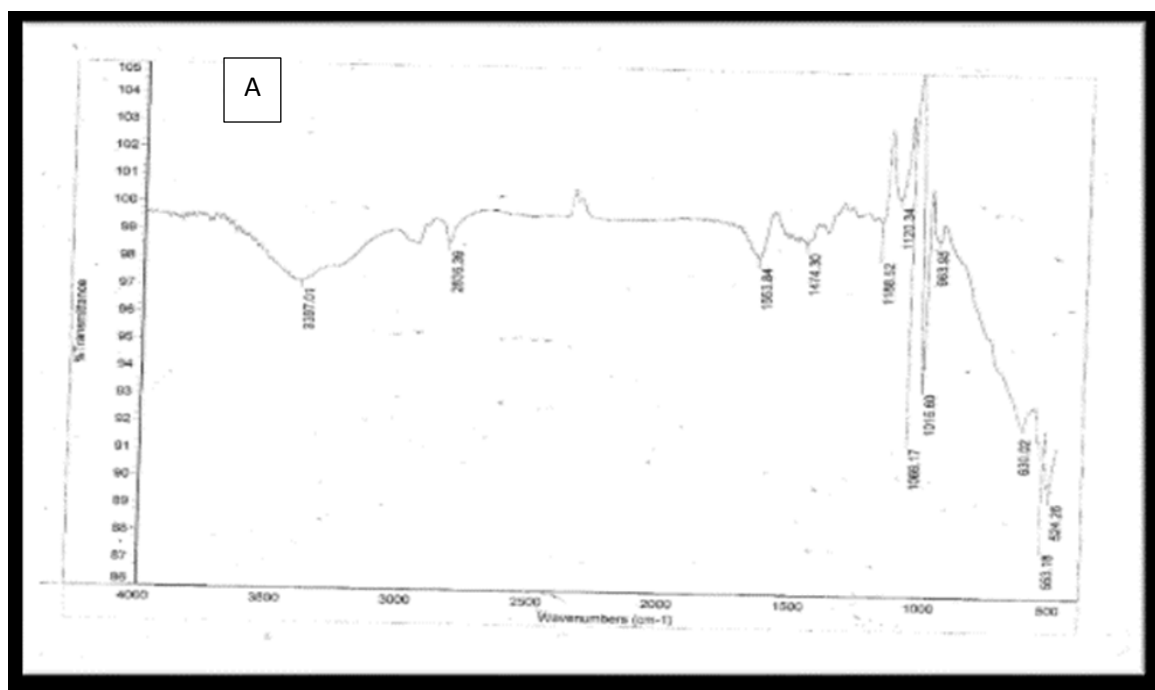


Figure 3.6: IR spectrum of CMC.



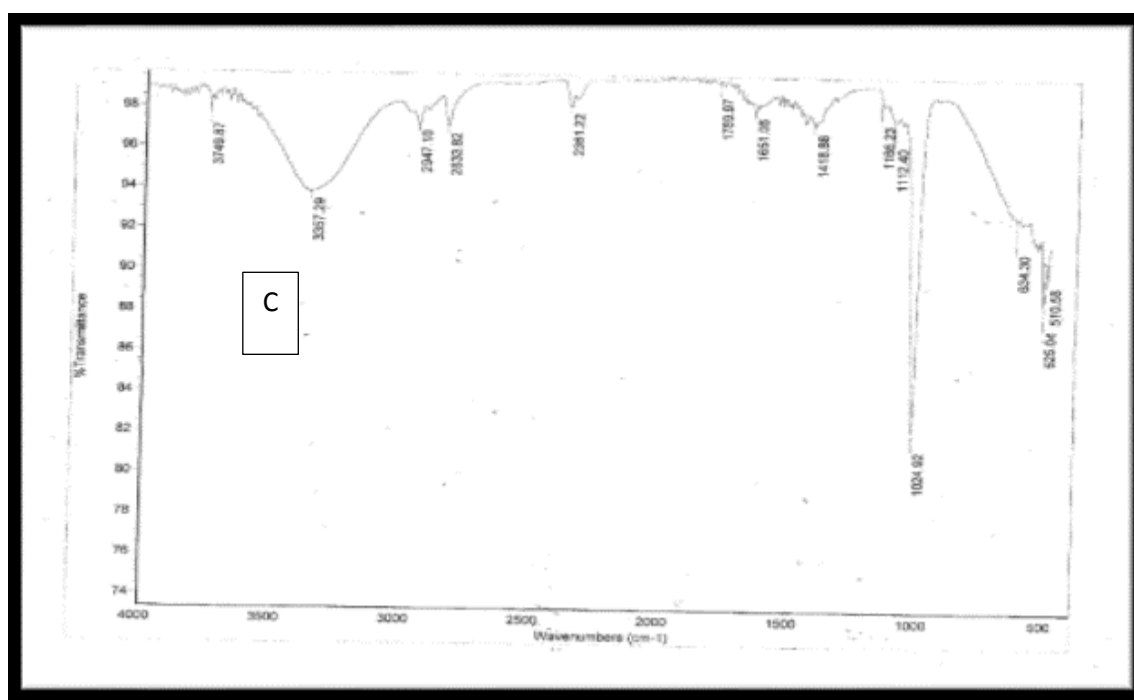
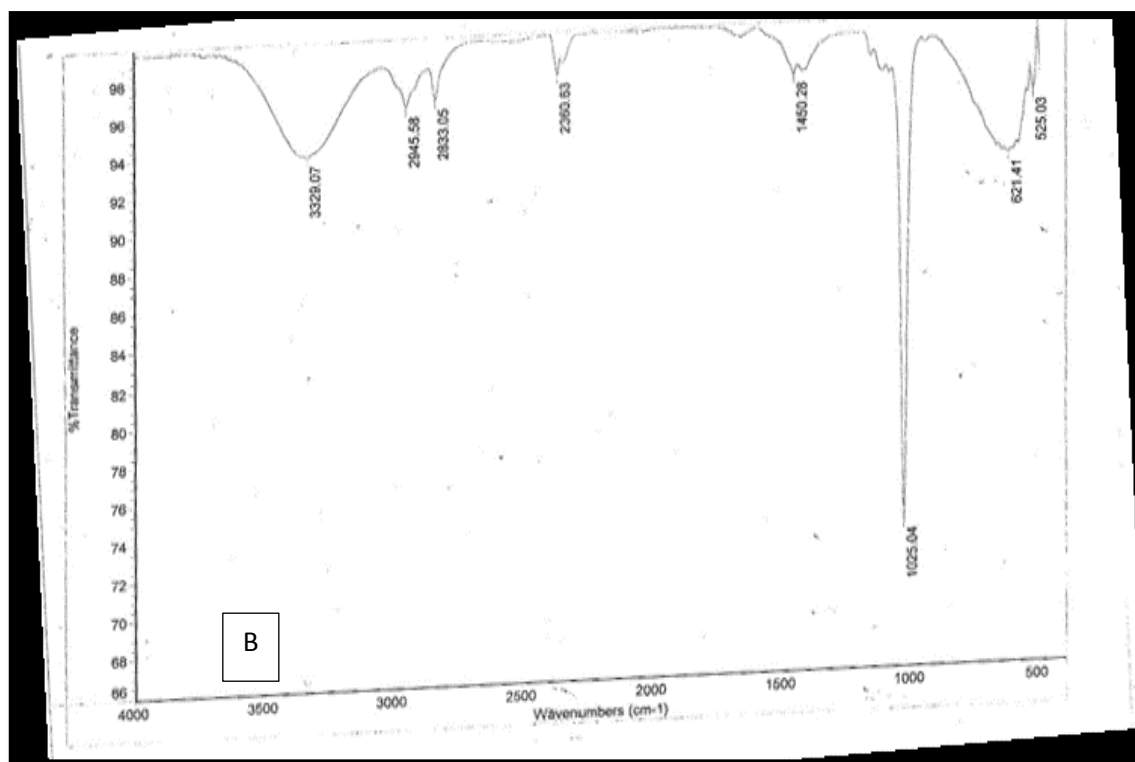


Figure 3.7: FT-IR spectrum of (a) CMC-CD-A, (b) CMC-CD-B and (c) CMC-CD-C.

3.3. Surface analysis by SEM

The obtained SEM images of polymers **CMC-CD-A**, **CMC-CD-B** and **CMC-CD-C** are shown in Figures 3.8, 3.9, and 3.10. Polymer obtained from mixing 1:3 ratio by weight of CMC and β -CD showed highest porosity, which could be attributed to the higher crosslinking density (% of crosslinked/repeat unit). Polymer obtained from mixing 1:1 ratio of CMC and β -cyclodextrin showed higher porosity. This could be related to crystallinity of CMC which overcomes the effect of crosslinking. However, the one prepared from mixing 3:1 ratio of CMC and β -cyclodextrin showed a hard-solid surface with little porosity

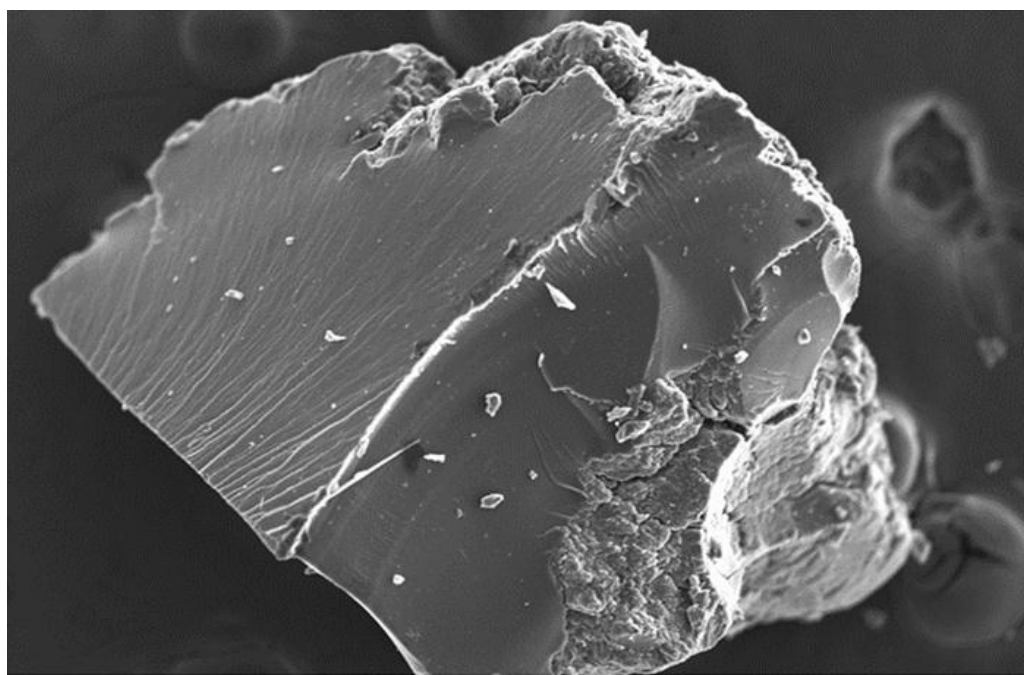


Figure 3.8: SEM images of polymer CMC-CD-A at 500x.

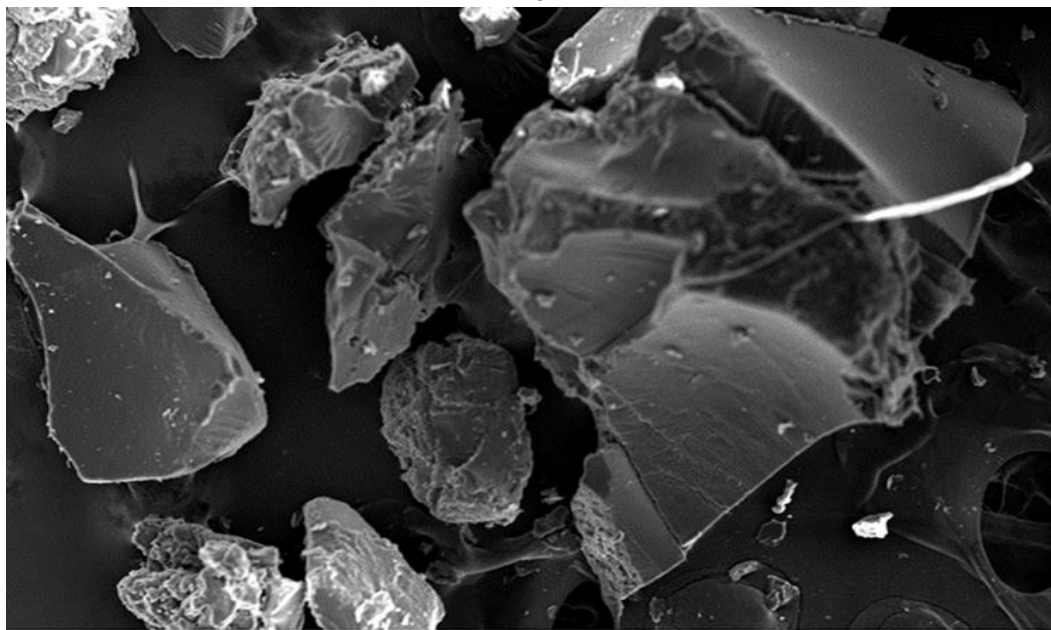


Figure 3.9: SEM images of polymer CMC-CD-B at 250x.

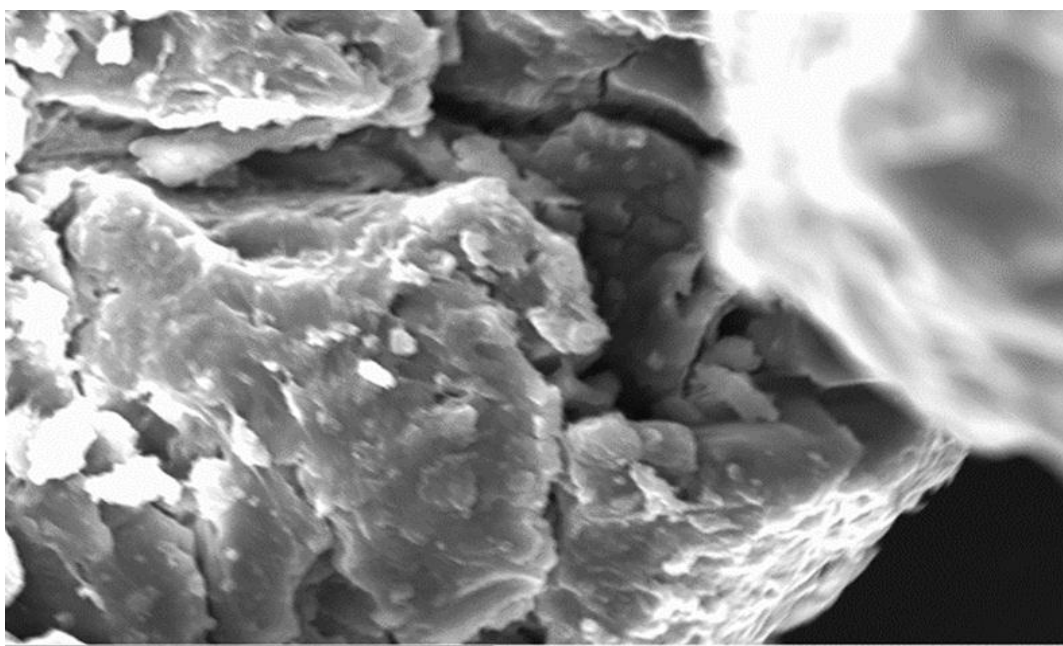


Figure 3.10: SEM images of polymer CMC-CD-C at 500x.

3.4. Effect of various parameters on adsorption efficiency

The objective of this study is to examine the efficiency of the new polymers as an adsorbent for toxic metals from wastewater. The adsorption behaviour of the new polymer toward the toxic metals was studied. The effect of various parameters such as pH, temperature, the amount of adsorbent, the concentration and the contact time on the adsorption efficiency of toxic metals were studied. The adsorption capacity was investigated kinetically. The equilibrium isotherm studies was carried out by varying the initial concentration of metal ions and adsorbent dose.

3.4.1 Effect of polymer dose on the adsorption efficiency

The effect of the adsorbed dose of polymers **CMC-CD-A**, **CMC-CD-B** and **CMC-CD-C** on present removal of Pb^{+2} from an aqueous solution was studied. The initial concentration of Pb^{+2} solution was maintained at 20.0 mg/L and solution volume at 10.0 mL, pH value was adjusted to 7.5 and temperature was kept at 20°C. The obtained results were summarized in figure (3.11).

The results demonstrated that, the present removal of Pb^{+2} by the crosslinked polymers increased by increasing the adsorbent dose from 0.005 to 0.05, the adsorption efficiency became constant. The equilibrium was reached with 0.05 g of adsorbent dose for the three polymers. This could be attributed to two factors: the limited number of the active sites and

the establishment of equilibrium in the concentration of Pb^{+2} between active solid phase and the liquid phase [40].

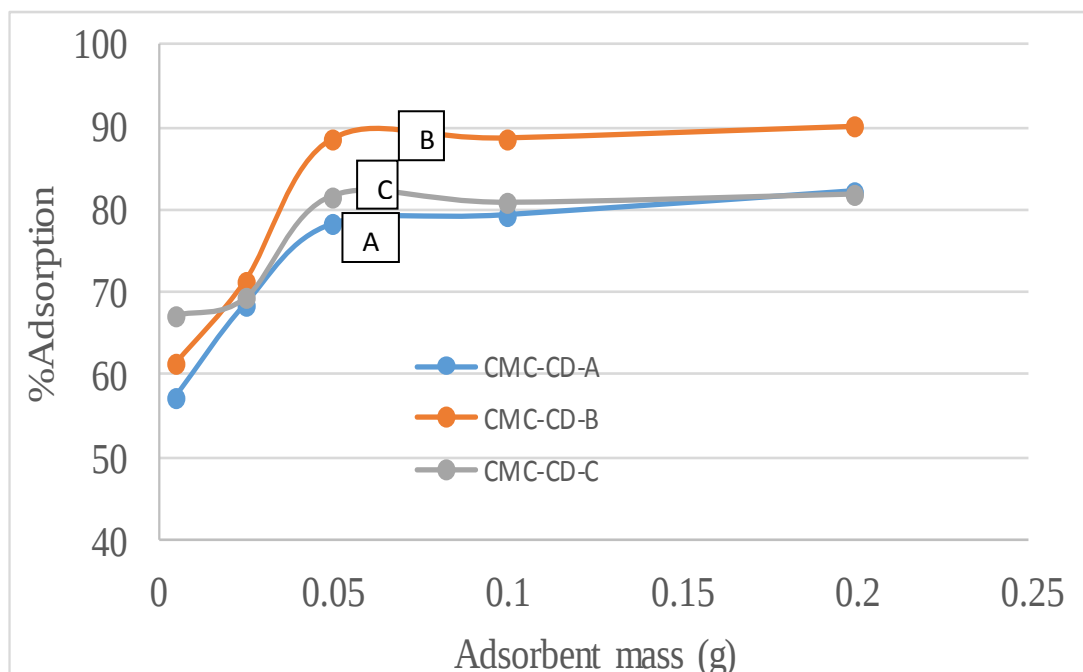


Figure 3.11: Effect of polymer dose on the adsorption efficiency of Pb^{+2} for polymer (A), ($C_i = 20 \text{ mg/L}$, $t = 30 \text{ min.}$, $T = 20^\circ\text{C}$, sol. Vol = 10 mL, pH = 7.5).

3.4.2 Effect of Pb^{+2} initial concentration on adsorption efficiency

An experiment was carried out to determine the optimum initial concentration of lead ion in a solution. A 0.05 g of a polymer adsorbent was added to a vial containing 10.0 mL of Pb^{+2} solution with various concentrations ranging from 1.0 to 50 mg/L, under optimized adsorption conditions. The results are shown in Figure (3.12) for the three polymer A. The results show that, the removal of Pb^{+2} was quantitative at low concentration, and didn't change until the initial concentration reached 50 mg/l. So, the optimum concentration was selected as 20 mg/L.

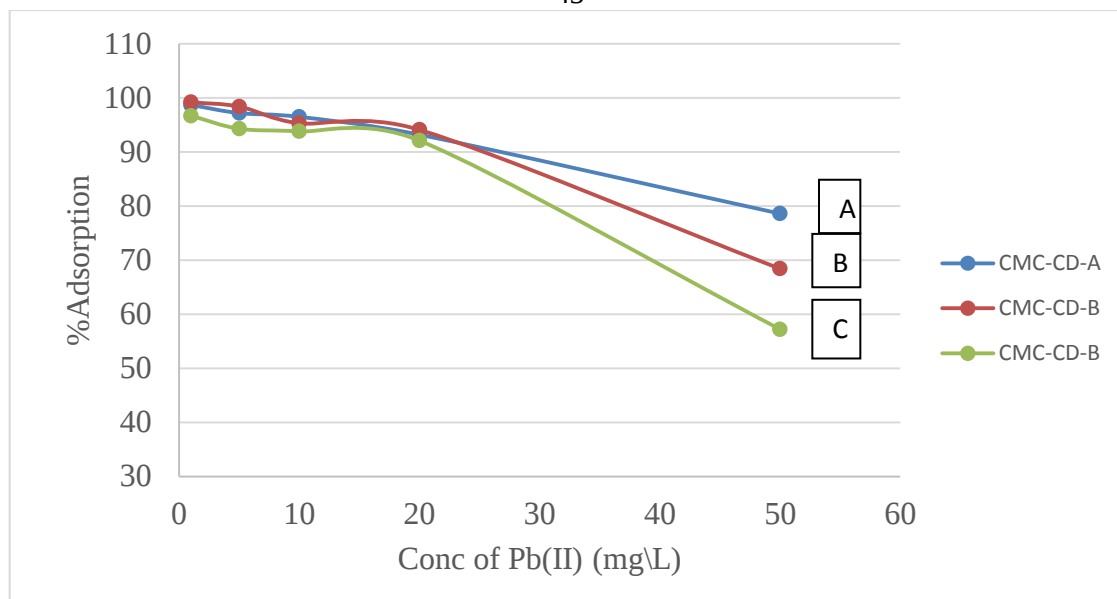


Figure 3.12: Effect of initial lead concentration on the adsorption efficiency of polymers CMC-CD-A, CMC-CD-B and CMC-CD-C (pH= 7.5, t = 30 min., T.= 30 °C, Vol = 10 mL, adsorbent dose = 0.05 g).

At low concentration, the binding sites are available at high numbers, but as the concentrations of Pb^{+2} increases, the available sites bind all metal ions [44]. So, initial concentration of 50 mg/L of Pb^{+2} the adsorption efficiency dropped to 78%, 68% and 57 % for polymer for CMC-CD-A, CMC-CD-B and CMC-CD-C, respectively.

3.4.3 Effect of Temperature on adsorption efficiency

The effect of temperature on the extraction of efficiency of the crosslinked polymers was evaluated at temperature range from 20 °C to 50 °C, the results are summarized in Figure 3.13. As shown in Figure 3.13, polymer CMC-CD-A and C showed some dependency on temperature. The efficiency of polymer **CMC-CD-A** increased as the temperature increased, indicating that, the complexation is the main factor in the adsorption

process. The efficiency of polymer **CMC-CD-C** decreased as the temperature increased, indicating that, the complexation process between metal ion and carboxyl group is exothermic. However, polymer **CMC-CD-A** showed less dependence on the temperature, indicating that, the complexation and inclusion factors are both present and the temperature showed opposite effect on them.

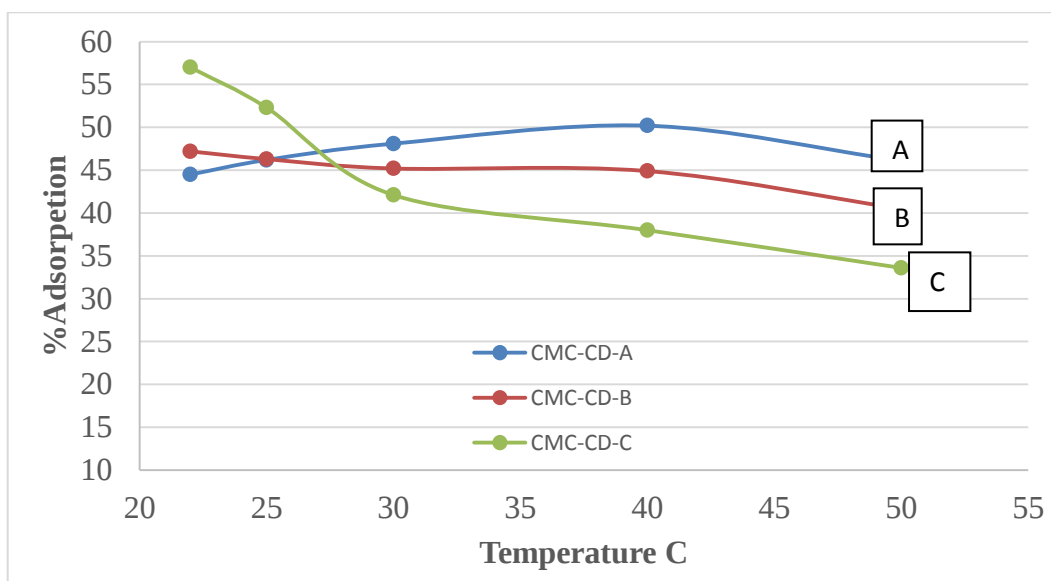


Figure 3.13: Effect of Temperature on the adsorption efficiency of Pb^{+2} for polymers. ($C_i = 20$ mg/L, $t = 30$ min., adsorbent dose = 0.05 g, Vol = 10 mL, pH 7.5).

3.4.4 Effect of pH value

The effect of the pH values on the efficiency of the polymers **CMC-CD-A**, **CMC-CD-B** and **CMC-CD-C** for the removal of Pb^{+2} from an aqueous solution was studied. The pH value is an important factor for adsorbents with ionic functional groups that might get protonated or deprotonated by raising or lowering the pH value [41]. The effect of the pH value on the adsorption capacity of the **CMC-CD-A**, **CMC-CD-B** and **CMC-CD-C**

polymers was carried out on solutions with various pH value ranging from 5 to 11.0. Figure (3.14) shows the obtained results.

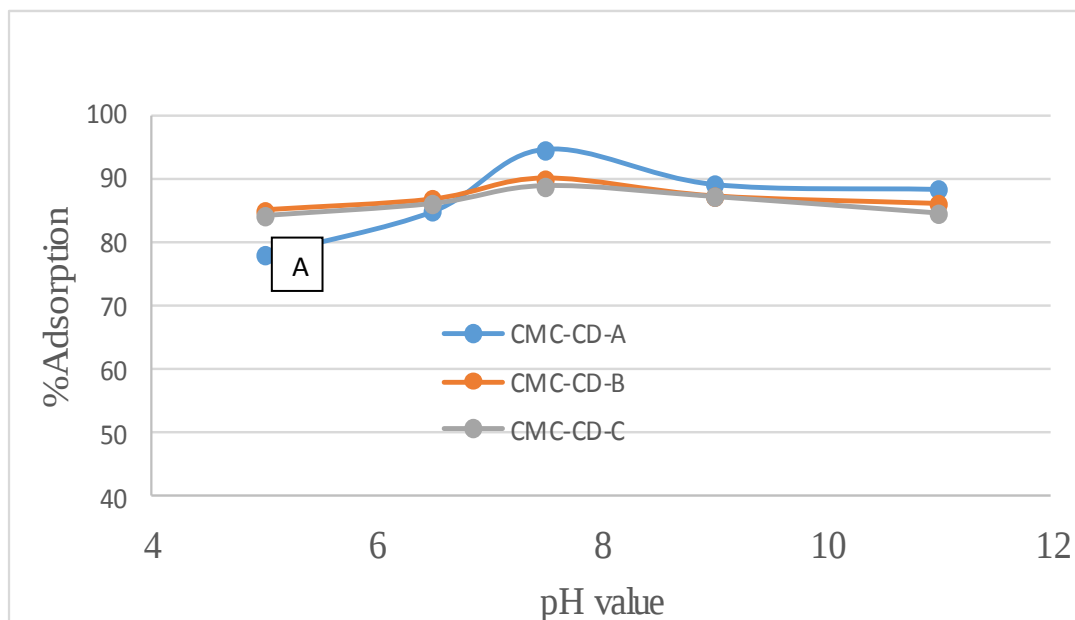


Figure 3.14: Effect of pH value on the adsorption efficiency of Pb^{+2} for the crosslinked polymers ($C_i = 20$ mg/L, adsorbent dose = 0.05 g, $T = 30$ °C, sol. Vol = 10 mL, $t = 30$ min).

Polymer **CMC-CD-A** showed the highest dependence on the pH value, this could be attributed even it has the lowest content of the carboxyl groups. The highest adsorbent rate was shown at a pH value of about 7.5. Lower removal rate was shown at low pH, which could be due to the presence of the carboxyl group in the protonated form [41].

3.4.5 Effect of contact time

The most effective adsorption time to achieve the maximum adsorption of Pb^{+2} from an aqueous solution by the prepared crosslinked polymers was determined. The results are summarized in Figure (3.15).

The three polymers showed almost similar adsorption trend with time. The fastest rate of adsorption occurred in the first 15 minutes, then it became steady, which could be attributed to the blocking of active sites by adsorbed metal ions. The active coordination and inclusion sites are available at large number at the beginning therefore high rate of adsorption occurs[36]. Then the rate becomes constant and indication that the active sites are saturated.

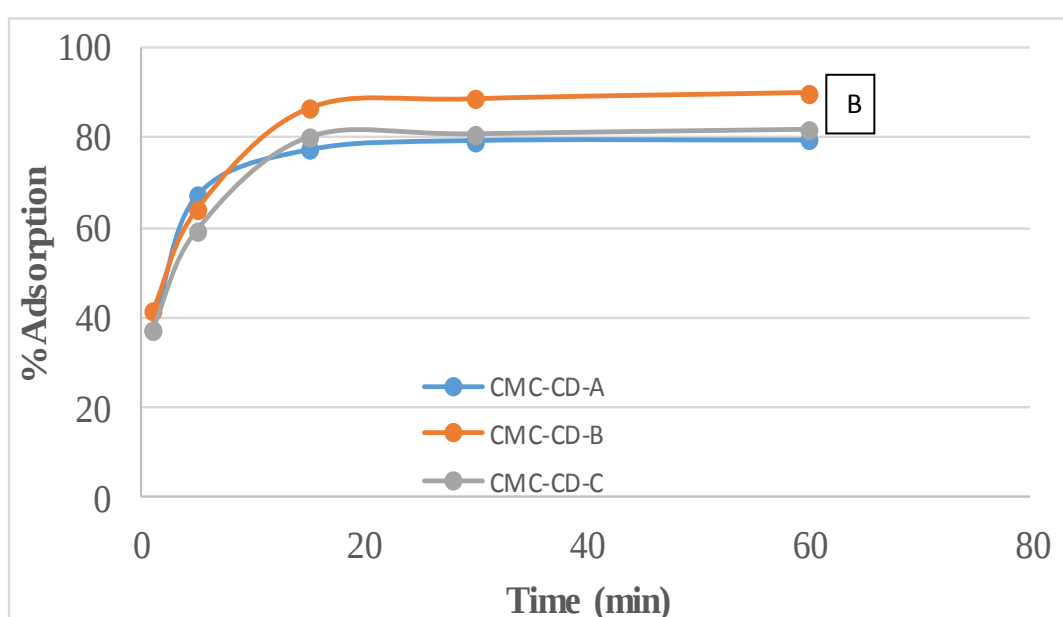


Figure 3.15: Effect of adsorption time on the adsorption efficiency of Pb^{+2} for three crosslinked polymers ($C_i = 20$ mg/L, adsorbent dose = 0.05 g., $T = 30^\circ C$, sol. Vol = 10 ml, pH = 7.5).

3.5 Adsorption Analysis

The Langmuir equation Eq. 3.1) and Freundlich isotherm equation (Eq. 3.2) were adapted to evaluate the type of metal ion distribution over the surface of crosslinked polymers after reaching the equilibrium at a constant temperature [42,43].

The Langmuir model presumes the formation of a single layer of metal ions on a homogeneous surface of an adsorbent [44]. While, the Freundlich model assumes a heterogeneous surface of adsorbents. Below is Eq. 3.1,

$$\text{Langmuir isotherm model: } \frac{C_e}{Q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max}K_L} \quad (3.1)$$

where C_e is the equilibrium concentration of metal ion (ppm), Q_e is the amount of adsorbate adsorbed per unit mass of cellulose amine at equilibrium (mg/g), Q_{max} is the theoretical maximum monolayer adsorption capacity of the adsorbent (mg/g), and K_L is the Langmuir isotherm constant related to the adsorption energy (L/mg). Equation 3.2 is as follows,

$$\text{Freundlich isotherm model: } \ln(q_e) = \ln k_f + \frac{1}{n} \ln C_e \quad (3.2)$$

where K_F and $\frac{1}{n}$ are empirical constants that indicate the relative adsorption capacity and intensity related to the affinity of the metal, respectively.

The Langmuir model also can be used to tell whether the adsorption was favourable or not by using the dimensionless constant factor shown in Eq. 3.3,

$$R_L = \frac{1}{1 + K_L C_0} \quad (3.3)$$

where K_L is the Langmuir constant and C_0 is the initial adsorbate concentration. The adsorption is unfavourable if the R_L value is higher than 1. However, if the value if R_L value is between 1 and 0, then the adsorption is favourable, and the adsorption is linear if R_L value is equal to 1.

All calculated parameters obtained are shown in Table 3.1. The coefficients for the Langmuir isotherm model shown in Table 3.1 were higher than those obtained from the Freundlich model. The results indicate that, the adsorption of Pb^{+2} follows the Langmuir model shown in Eq. 3.1. The results indicate that, the Pb^{+2} are homogeneously distributed over CMC-CD-A surfaces. The R_L factor, was found to be $0 < R_L < 1$ (Table 3.1), that is much smaller than, meaning a high affinity of CMC-CD-A for Pb^{+2} .

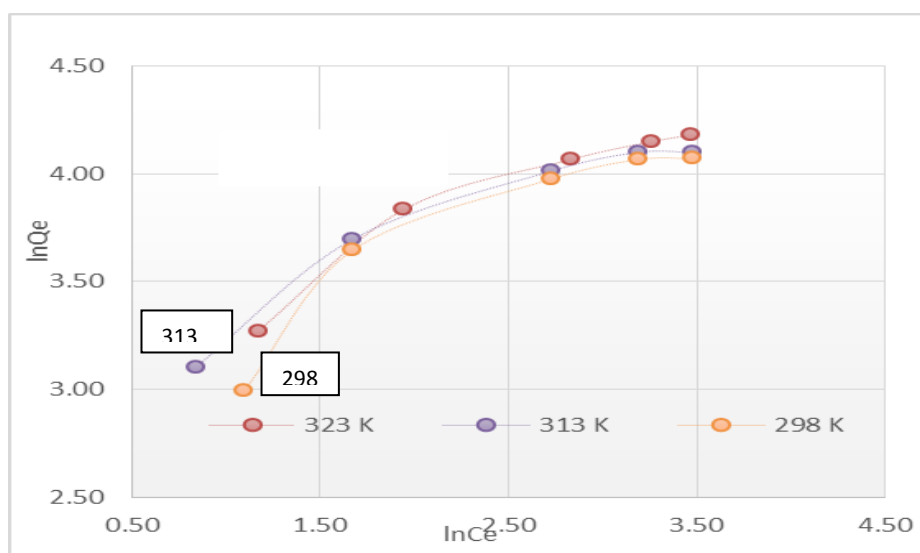


Figure 3.16: Langmuir adsorption of Pb^{+2} on CMC-CD-A polymer at various temperatures.

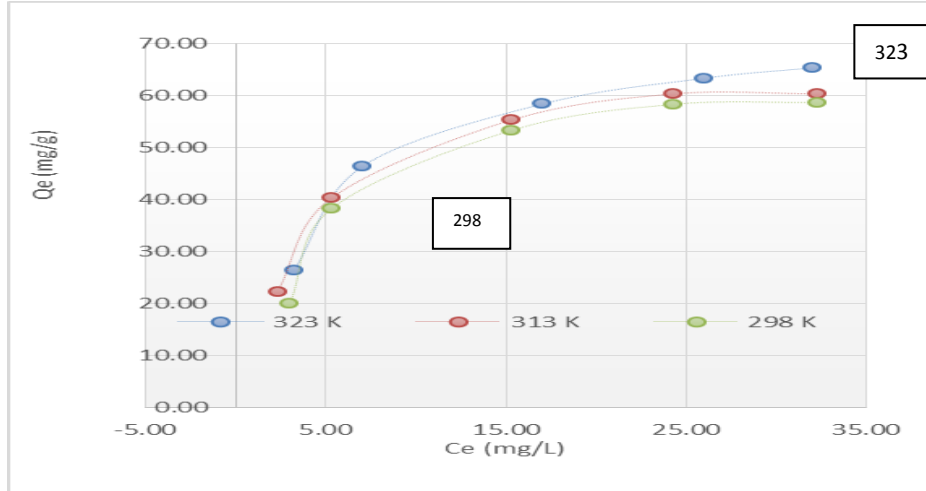


Figure. 3.17. Freundlich adsorption of Pb^{+2} on CMC-CD-A polymer at various temperatures

Table 3.1: Langmuir and Freundlich Parameters for the Adsorption of Pb^{+2} on CMC-CD-A.

Pb^{+2}				
Temperature (K)		298.0	313.0	323.0
Langmuir Isotherm	Q^0 (mg/g)	2.4163	2.1475	2.3971
	K_L (L/mg)	0.1048	0.1109	0.1047
	R_L	0.01901	0.0169	0.01901
	R^2	0.9801	0.8691	0.977
Freundlich Isotherm	$1/n$	0.9112	0.7151	0.832
	K_F (L/mg)	20.4661	26.230	24.375
	R^2	0.945	0.9867	0.9762

3.5.1 Kinetics Adsorption

The kinetic models, pseudo-first-order (Equation 3.4) and pseudo-second-order (Equation 3.5), were used to study the kinetics of the adsorption of Pb^{+2} onto the polymer surface[45-46]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (3.4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3.5)$$

The intraparticle diffusion model (Equation 3.6) was also used to reveal the rate-determining step during the Pb^{+2} adsorption,

$$Q_t = K_{id}t^{\frac{1}{2}} + Z \quad (3.6)$$

where Q_e and Q_t are the adsorption capacities at equilibrium (mg/g), t is the various times (min), K_1 is the pseudo-first-order rate constant (1/min), K_2 is the pseudo-second-order rate constant (g/mg min), K_{id} is the intraparticle diffusion rate constant ($\text{mg/gmin}^{1/2}$), and Z (mg/g) was used to conclude the thickness of the boundary layer.

The liquid film diffusion model (Equation 3.7) was used to determine if the Pb^{+2} transport between the liquid phase and the solid phase plays a role in the adsorption process,

$$\ln(1 - F) = -K_f dt \quad (3.7)$$

where F is the fractional attainment of equilibrium ($F = q_t/q_e$), q_e is the adsorption capacity of the sorbent at equilibrium ($\text{mg} \times \text{g}^{-1}$), and K_f is the liquid film diffusion constant. A plot of $\ln(1-F)$ vs t with zero intercept would mean that the kinetics of the adsorption process was regulated by diffusion from the liquid phase to the polymer structure.

The values of all calculated parameters using the above equations are shown in Table 3.1 and Figure 3.17.

The value of K_1 was determined from plotting $\ln(q_e - q_t)$ vs. t as shown in Figure 3.18.

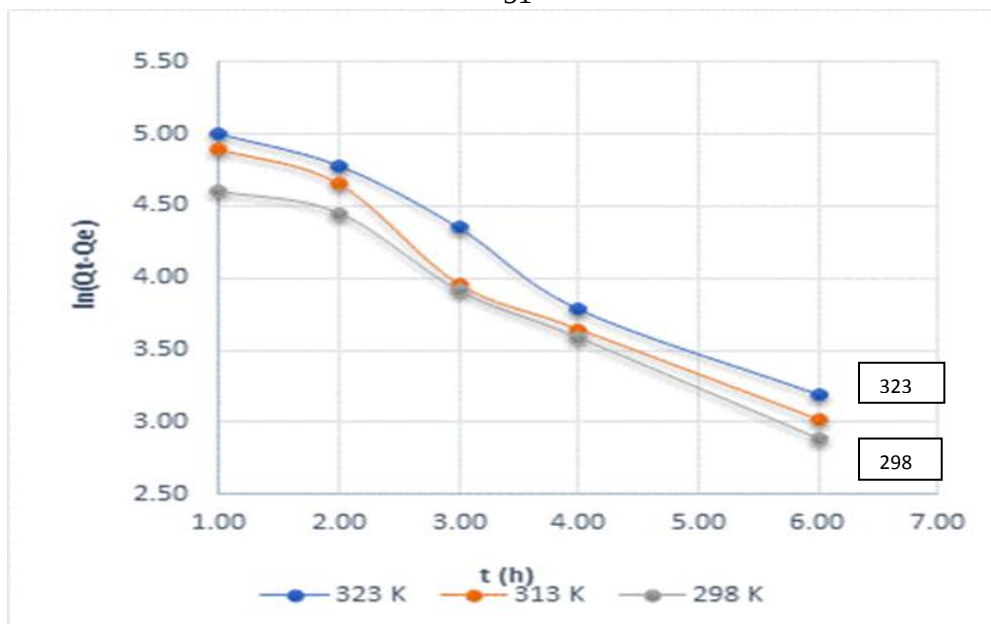


Figure 3.18: Pseudo first-order model for the adsorption of Pb^{+2} .

The K_2 values and the adsorption capacity (q_e) were determined from the slope and the intercept of plot shown in Figure 3.19.

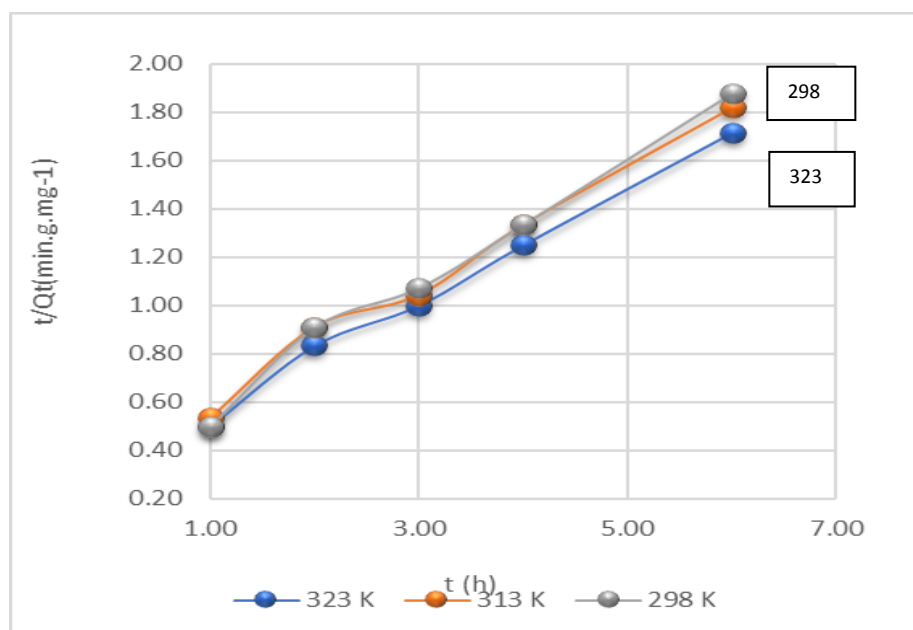


Figure 3.19: Pseudo-second order model for the adsorption of Pb^{+2} onto CMC-CD-A.

The K_{id} and Z values were determined from plotting qt vs. $t^{1/2}$ as shown in

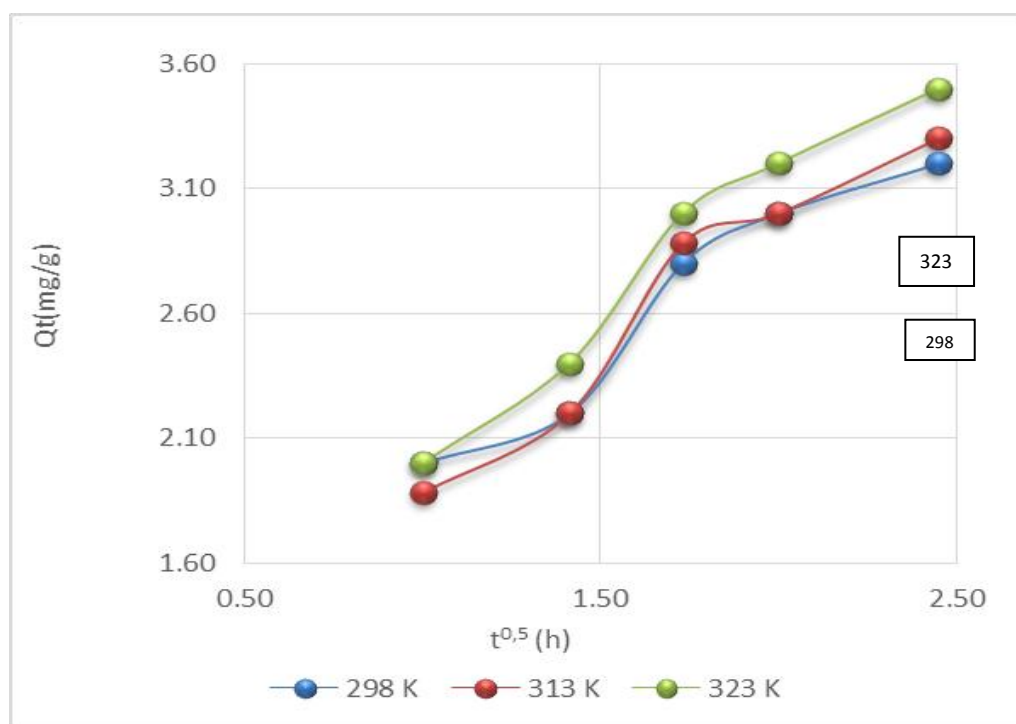


Figure 3.20: Intra-particle diffusion for the adsorption of Pb^{+2} by CMC-CD-A polymer at different concentrations of Pb^{+2}

The obtained R^2 for the pseudo-second-order was 0.9808 to 0.9901) were higher than the pseudo-first-order (0.862). The q_e values shown in Table 3.12 (151.2, 195.9 and 231.0) were close to the experimental q_e values (147.6 mg/g, 191.2 mg/g, and 228.6 mg/g). The results indicates that, the adsorption process of Pb^{+2} ions on the surfaces of CMC-CD-A follows the pseudo-second-order.

Table 3. 2. The Pseudo-second-order Model for Adsorption of Pb^{+2} by CMC-CD-A

T (K)	298			313			323		
	K_2 (g/mg $\times$ min)	Q_{cal} (mg/g)	R^2	K_2 (g/mg $\times$ min)	Q_{cal} (mg/g)	R^2	K_2 (g/mg $\times$ min)	Q_{cal} (mg/g)	R^2
Pb^{+2}	0.3655	151.2	0.9901	0.3897	195.9	0.9801	0.3793	231.0	0.9808

Table 3. 3. The Intraparticle Diffusion Parameters of Pb^{+2} onto polymer CMC-CD-A

T (K)	298			313			323		
	K_{id}	Z	R^2	K_{id}	Z	R^2	K_{id}	Z	R^2
Pb^{+2}	0.910	1.09	0.941	1.042	0.875	0.953	1.090	0.95	0.958

Plots shown in Figures 3.18 to 3.20 did not pass through the origin. This indicate that there is more than one rate-determining step in the adsorption processes [47]. The Z values shown in Table 3.12 indicate an expansion in the layer exposed to the liquid phase and the potential for internal mass transfer is high.

The mechanism for the removal of Pb^{+2} via adsorption occurred in a multistep process. Initially, the Pb^{+2} migrate from the liquid phase to the adsorbent layer exposed to the liquid. This controlled by the diffusion to the active sites. Finally, intraparticle diffusion and complexation of Pb^{+2} with the active sites occurs. The valid mechanism was examined by the liquid-film and the intraparticle-diffusion models. The liquid-film diffusion model (Equation 3.9) suggests that, a linear plot of **$\ln(1 - F)$ vs. t** with a zero intercept indicates that the kinetics of the adsorption process were

controlled by diffusion from the surrounding liquid film to the polymer surface. As shown in Figure 3.21, the straight lines did pass through the origin, and had a coefficient of 0.1569 for Pb^{+2} ($R^2 = 0.9943$). This means that the diffusion of the metals through the surrounding liquid film near the CMC-CD-A surface was not the rate-determining step, but could contribute to the adsorption process.

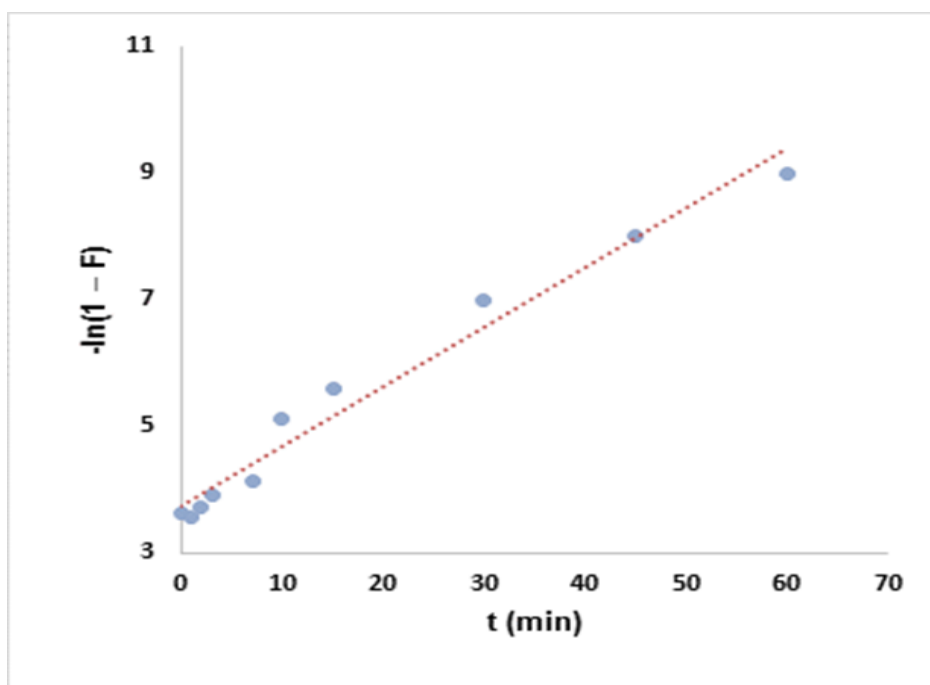


Figure 3.21: Liquid film diffusion model plots for the adsorption of Pb^{+2} by CMC-CD-A.

3.5.2 Adsorption Thermodynamics

The Gibbs free energy (ΔG_0), enthalpy (ΔH_0), and entropy (ΔS_0) were calculated using the following equations 3.8 to 3.10 , The obtained values are summarized in Table 3.4.

$$K_c = \frac{C_{ads}}{C_e} \quad (3.8)$$

$$\Delta G^\circ = -RT \ln K_c \quad (3.9)$$

$$\ln K_s = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3.10)$$

K_c is an apparent constant of the thermodynamics, C_{ads} is the amount adsorbed at equilibrium (mg/L), C_e is the equilibrium concentration in an aqueous solution of metal ion (mg/L), R is the gas constant (J/mol $\times$ K), and T is the ions solution temperature K [43] .

Table 3.4: Thermodynamic Parameters for the Adsorption of lead ions onto CMC-CD-A.

T(K)	Pb(II)		
	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol)
298	-18.6156	16.4161	77.9326
313	-19.5535		
323	-20.1787		

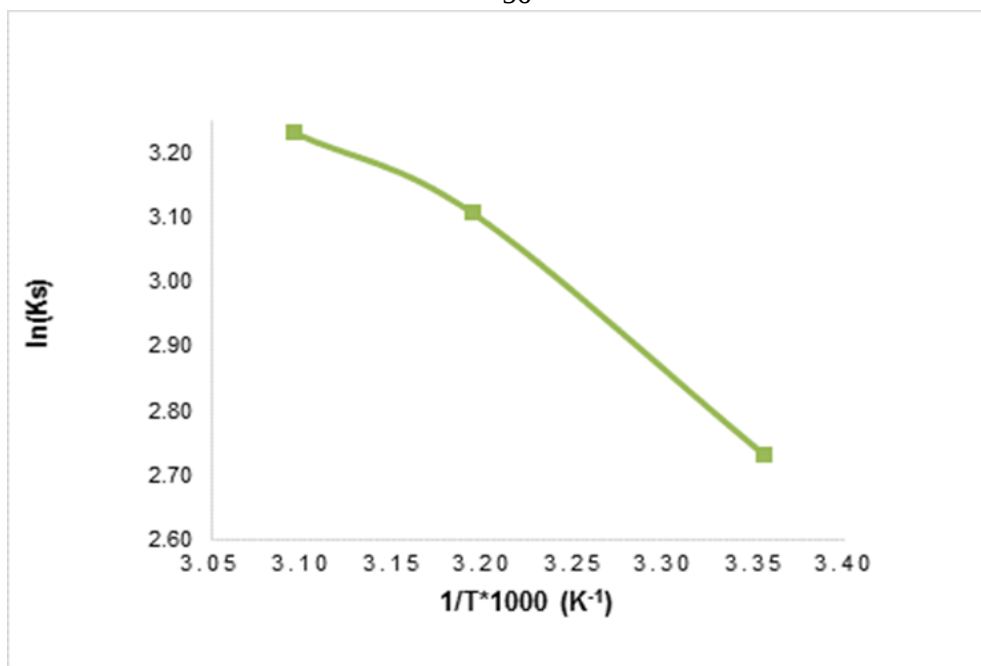


Figure 3.22: Thermodynamic study of adsorption of Pb^{+2} onto CMC-CD-A

The K_c value was calculated using the Van't Hoff equation shown in Equation 3.8 [48]. The ΔG_0 value (Jmol^{-1}) was calculated using Equation 3.9. The $\ln(K_s)$ vs T^{-1} was plotted as shown in Fig 3.22. The determined slopes and the intercept were used to calculate other thermodynamics parameters. Results are summarized in Table 3.4. The ΔS_0 and ΔH_0 values were positive, the entropy increased at the adsorbent/liquid interface, driven by the adsorption process. The ΔG_0 value was negative, indicating a spontaneous adsorption process.

Conclusions

1. Cross-linked polymers (CD-CA-A, B, and C) were synthesized using CMC and β -cyclodextrin. Various compositions of CMC and β -cyclodextrin were used in the synthesis of the three polymers.
2. The prepared polymers were analyzed by FT-IR and SEM.
3. The prepared polymers were successfully used for adsorption of Pb^{+2} from wastewater. Removal of Pb^{+2} from waste water by three polymers reached were quantitative. The results also indicates that, the adsorption process of Pb^{+2} on the surfaces of CMC-CD-A follows the pseudo-second-order.
4. Thermodynamic studies showed that the ΔG_0 value for the adsorption process was negative, indicating a spontaneous adsorption process.

Recommendations

- a .More investigation is required to prepared polymers with new CMC / β -cyclodextrin ratios.
- b. These polymers can be investigated in water treatment from organic pollutants..
- c. The preparation of polymers of Cellulose can be studied using substances other than β -cyclodextrin , or other cross-linking agents .
- d. These polymers can be investigated in various applications in different areas of drug administration and the pharmaceutical industry.

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كلية الدراسات العليا

نقية مياه الصرف الصحي من عنصر الرصاص بواسطة بلورات صغيرة جدا
من السليولوز الايوني

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بإشراف

د.عثمان حامد

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء، بكلية
الدراسات العليا، في جامعة النجاح الوطنية، نابلس - فلسطين.

2020

ب

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إعداد

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بإشراف

د. عثمان حامد

د. احمد ابو عبيد

الملخص

تتعرض مصادر المياه الصالحة لشرب على هذا الكوكب للتلوث بالمعادن السامة والمواد العضوية. ويرجع السبب إلى انتشار الصناعات المختلفة وتتطور الحياة. هذه المواد السامة الموجودة في الماء خطيرة يمكن أن تسبب ضرراً دائماً للحياة على الأرض. تركز الأبحاث الحالية على تطوير طرق لإزالة هذه المعادن السامة من الماء، حيث تم تطوير العديد من الطرق الكيميائية لتنقية المياه، وطرق التنقية البسيطة والصديقة للبيئة أكثر فعالية.

السليولوز هو واحد من أكثر البوليمرات الطبيعية وفرة، ولديه العديد من المزايا التي تجعله مرشحاً فعال لاستخدامه في عمليات التنقية هذه، كرخص ثمنه، توافره، امن على البيئة، والقابلية للتحلل البيولوجي مما يجعل البوليمر صديقاً للبيئة.

في هذه الدراسة تم استخدام السليولوز كمادة أساسية في تشكيل بوليمر ليتم استخدامه في تنقية المياه من المعادن السامة وبشكل اساسي الرصاص , اولا تم تحويل السليولوز إلى كاربوكسل ميثل سليولوز

عن طريق تفاعل السليولوز مع كلور أسيتات ومحلول هيدروكسيد الصوديوم في كحول الأيزوبروبيل. تم ربط CMC الناتج مع البييتاسايكلوديكسترين بوضعها بالفرن على حوالي 160 درجة مئوية.

تم تحضير ثلاثة بوليمرات من تلك المواد (co- β -CMC-CD) A, B and C باستخدام نسب مختلفة. تم تحليل تراكيب البوليمرات بواسطة FT-IR ودرس شكل وبناء البوليمر بواسطة المسح الضوئي الإلكتروني. تم التحقق من كفاءة الامتصاص لثلاث بوليمرات لعنصر الرصاص Pb(II) في محلول مائي، مع دراسة اثر العديد من العوامل على فعالية إزالة عنصر الرصاص من المياه، وهذه العوامل هي: كمية البوليمر، والوقت الذي تعرضت له المياه الملوثة بالرصاص للبوليمر، ودرجة الحرارة، وتركيز محلول الرصاص ودرجة الحموضة، وذلك للتوصل للظروف المثالية التي تؤدي الى أقصى فعالية في إزالة عنصر الرصاص من المياه.

البوليمر اظهر كفاءة عالية في ازالة عنصر الرصاص من المياه عند ظروف (درجة الحموضة 7.5، درجة حرارة الغرفة، التحريك لمدة 30 دقيقة، وتركيز 5.0 جزء لكل مليون.

يمكن أن تعزى كفاءة الامتصاص العالية لبوليمرات السليولوز إلى وجود العديد من المجموعات الوظيفية

الموجودة في كل بوليمر بما في ذلك الهيدروكسيل , الكربوكسيل و بيتا سايكلوديكسترين .أظهر البوليمر B الذي يحتوي على كميات متساوية من β -cyclodextrin and CMC كفاءة أعلى قليلاً تجاه الرصاص (II) من البوليمران الآخران. يمكن أن يكون هذا بسبب توافر كل من المجموعات الوظيفية كربوكسيل وبيتا سايكلوديكسترين. تشير هذه النتائج إلى أن عملية الدمج والتعقيد هي بنفس القدر من الأهمية في عملية الامتصاص.

تشير النتائج إلى أن هذا العمل يقدم طريقة سهلة لصنع مادة ممتصة بكفاءة عالية

