An-Najah National University

Faculty of Graduate Studies

Cross-Linked β-Cyclodextrin for Removal of Toxic Metals from Wastewater

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Dedication

"With hard work and dedication, anything is possible". *Timothy Weah*

To my family, my mom and dad ... my loved ones my children Careem and Ahmed. To my colleagues, and my friends.

To all of them I dedicate this work.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Cross-Linked β-Cyclodextrin for Removal of Toxic Metals from Wastewater

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يُقدم لنيل أية 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.

Student's name: **اسم الطالب:**

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Date: **التاريخ:**

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List of Abbreviations

Symbol	Abbreviation
CA	Citric acid
C_e	Concentration of metal ions in the sample solution after treatment at equilibrium (mg/L)
C_o	Initial concentration of metal ions in the sample solution (mg/L)
CyDs	Cyclodextrins
DMSO	Dimethylsulfoxide
FT-IR	Fourier Transform Infrared
K_1	The Lagergren's first order rate constant
K_2	The pseudo second order rate constant
K_F	Freundlich constant which is an approximate indicator of adsorption capacity of the sorbent (mg/g $(L/mg)^{1/n}$)
K_L	Langmuir isotherm constant (L/mg)
n	Dimensionless Freundlich constant giving an indication of how favorable the adsorption process
NMP	N-methyl pyrrolidone
pKa	Dissociation constants of acid
PYR	2-pyrrolidone
q_e	The amount of MB dye adsorbed per gram of the adsorbent (mg/g)
q_m	Maximum monolayer coverage capacity (mg/g)
q_t	Amount of adsorbate per unit mass of adsorbent at time t (min)
R	The gas constant (8.314 J/mol K)
R^2	Correlation coefficient (regression coefficient)
R_L	Dimensionless constant separation factor
SPE	Solid Phase Extraction
SEM	Scanning Electron Microscope
t	Time
T	The absolute temperature (^oK)
V	Volume of solution
w/v	The amount by weight (mass) of a solid substance dissolved in a measured quantity of liquid.

WHO	World Health Organization
α-CyD	Alpha Cyclodextrin
β-CyD	Beta Cyclodextrin
(co-β-CyDe-CA)	β-cyclodextrin cross-linked with citric acid
γ-CyD	Gama Cyclodextrin

Cross-Linked β-Cyclodextrin for Removal of Toxic Metals from Wastewater

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Abstract

Water is one of the essential renewable resources to preserve all forms of life. Human activities has an counter effect on the bodies of water. Water contamination occurs by addition of dangerous chemicals or foreign substances to water. The need to maintain a cleaner environment for the survival of aquatic and terrestrial lives is very important that increasingly concerns the ecologist. The most serious problem is environmental pollution of heavy metals and minerals in wastewater. So using adsorbents to remove toxic metals ions from contaminated water is necessary since they cause disruption to human organelles as they are a non-biodegradable contaminant.

β-Cyclodextrin (β-CyD) is cyclic oligosaccharide composed of 7 glucopyranose units linked by glycosidic bonds. It is a water-soluble carbohydrate with high performance for absorbing organic matters. In this work, β-cyclodextrin was modified to be insoluble in water and used in wastewater purification. The crosslinking will be carried out by reacting β-cyclodextrin with the polycarboxylic citric acid. The cross-linking adds a new functionality to β-cyclodextrin which is carboxyl groups. This modified β-cyclodextrin is a very good candidate to be used in wastewater

purification from both metals and organic materials. The cross-linked β-cyclodextrin polymer was prepared by two methods A & B. The same procedure used for preparing the two polymers; the only difference is the amount of citric acid was three times the amount of beta-cyclodextrin in the polymer (B), while the quantities were equal in the polymer (A).

The new cross-linked β-cyclodextrin (co-β-CyDe-CA) was successfully prepared. Fourier Transform Infrared (FT-IR) results confirm the formation of the cross-linked β-cyclodextrin polymers (A, B). The removal experiments of toxic metal ions were carried under a wide range of pH, adsorbent dosage, temperature, initial concentration and contact time. Over 98% removal efficiency of the prepared polymers was achieved after 180 min, at pH around 9 and temperature about 30°C using 0.1 g weight of dosage and initial concentration of 50 mg/L of 10 mL of lead ions aqueous solution. The experimental results show that (co-β-CyDe-CA) was able to almost completely removes Pb(II) rapidly in the first few minutes with high efficiency. Under best conditions and room temperature the removal was the highest.

It was found that removal of toxic metal ions from aqueous solution using the prepared polymers was explained well by Freundlich model (R^2= 0.99). This model describes the adsorption on to the heterogeneous surfaces possessing adsorption sites with different affinities.

Toxic metal ions removal by using the prepared polymers can be described by pseudo second order isotherm model. The pseudo second order model well represented the removal kinetics of both polymer (B), and polymer (A). The $qe_{(calc.)}$ value that obtained by this model was almost equal to the $qe_{(exp.)}$ an indication that the limiting step.

Chapter One
Introduction

1.1 General Review

Water is one of the essential renewable resources to maintain all forms of life, food production, economic development and for the general welfare. It is truly a unique gift for the humankind from nature. Water is one of the most manageable natural resources, since it is capable of diverting, transporting, storing and recycling. The country's area and groundwater resources play an important role in agriculture, hydroelectric power generation, livestock production, industrial activities, forestry, fishing, navigation, recreational activities, etc. [1].

Human activities including industrialization and agricultural practices, contributed enormously to the degradation and pollution of the environment, which has an adverse effect on the bodies of water that is a necessity for life [2].

Pollution occurs through the addition of contaminants into a natural soruces. Toxic substance present as contaminants affects more than two hundred million people on earth, according to Pure Earth (non-profit environmental organization). Water pollution occurs when dangerous foreign substances inter the water stream and that include chemicals, pesticides and fertilizers from agricultural, or metals such as lead or mercury [3].

The world health organization (WHO) reports that 80% of diseases are transmitted by water. Industrialization, the discharge of domestic waste, radioactive waste, and population growth, excessive use of pesticides, fertilizers and leaking water tanks are the main sources of water pollution. These wastes have negative effects on human health [4].

The need to maintain a cleaner environment for the survival of aquatic and terrestrial lives, including humans, is very important and is an issue that increasingly concerns the ecologist. The contamination caused by agents such as heavy metals and dyes is among the list that made the environment harmful and represented a serious health problem for the population [5]. The control of water pollution has reached paramount importance in developed countries and in several developing countries. The prevention of pollution at source, the precautionary principle and the prior authorization of wastewater discharges by the competent authorities have become key elements of successful policies to prevent, control and reduce the inputs of hazardous substances, nutrients and other water pollutants from point sources to aquatic ecosystems [6].

Water pollution can occur from two sources; point source and non-point source. Point sources of pollution include wastewater effluents (both municipal and industrial) and storm sewer discharges, which mainly affect the nearby area. While the sources of non-point pollution are those that come from different sources of origin and the number of ways in which the

pollutants enter the ground or surface water and reach the environment from different non identifiable sources [1].

Wastewater results by the introduction of certain substances which render it unsafe for some purposes such as drinking and plants watering. The day to day activities of man is mainly water dependent and therefore discharge ‘waste’ into water. It is known that much of water supplied ends up as wastewater which makes its treatment very important [7].

The most serious problem is environmental pollution, particularly of heavy metals and minerals in wastewater due to extensive anthropogenic activities, such as industrial operations, in particular mining, agricultural processes and the disposal of industrial waste; their concentration has increased to dangerous levels [8]. The presence of inorganic contaminants such as metal ions like Ni^{2+}, Pb^{2+}, Cr^{6+} in water, probably due to long-term geochemical changes and effluents from various industries, causes diseases and disorders, such as cancer, neurodegenerative diseases, muscular dystrophy, hepatitis and multiple sclerosis [9]. Transition metal ions such as arsenic, copper, cadmium, chromium, nickel, zinc, lead, and mercury are major pollutants of fresh water reservoirs because of their toxic, non-biodegradable, and persistent nature [10]. The removal of toxic metals from wastewater is necessary because they disrupt the human organelles, consumed through the food cycle as non-biodegradable contaminants [9].

Adsorption is a fundamental process in the physicochemical treatment of municipal wastewaters, a treatment which can economically meet

today's higher effluent standards and water reuse requirements. Adsorption is integral to a broad spectrum of physical, biological, and chemical processes and operations in the environmental field [11]. Several researchers are widely using the adsorption processes for the removal of heavy metals from waste streams and activated carbon has often been used as an adsorbent. In recent years, the need for safe and economical methods for the removal of heavy metals from contaminated water has required a research interest in the production of low cost alternatives to commercially available activated carbon [12].

Recently Solid Phase Extraction (SPE) technique has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes. The SPE has several major advantages that include higher enrichment factor, simple operation, safety with respect to hazardous samples, high selectivity, lower cost and less time, and the ability to combine with different modern detection techniques [13].

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 [14]. The large number of the hydroxyl groups in cyclodextrins are considered binding sites and able to form various types of linkages. A cross-linking with other compounds or polymers, or their derivatization are considers the main reactions of these

cyclodextrins. Moreover, they are able to form complexes with polymers and varius substrates, thus changing their physicochemical properties [15].

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 [14].

In this work, β-CyD was converted to be insoluble in water so we can use it 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 (160^{o}C). At this temperature, citric acid will be 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.

1.2 Structure and Properties of cyclodextrins

The macrocyclic cyclodextrins which is produced by enzymatic hydrolysis of starch were discovered in 1891, and the structures were determined in 1930. Their industrial applications became important in 1970s, and now

thousands of metric tons of the three cyclodextrins (α-, β-, and γ-CyD) and are produced annually [16]. The three α-, β- and γ-cyclodextrin consist of six, seven, and eight glucopyranose units, respectively, known as parent cyclodextrins, there structures are shown in Figure. 2.1[17].

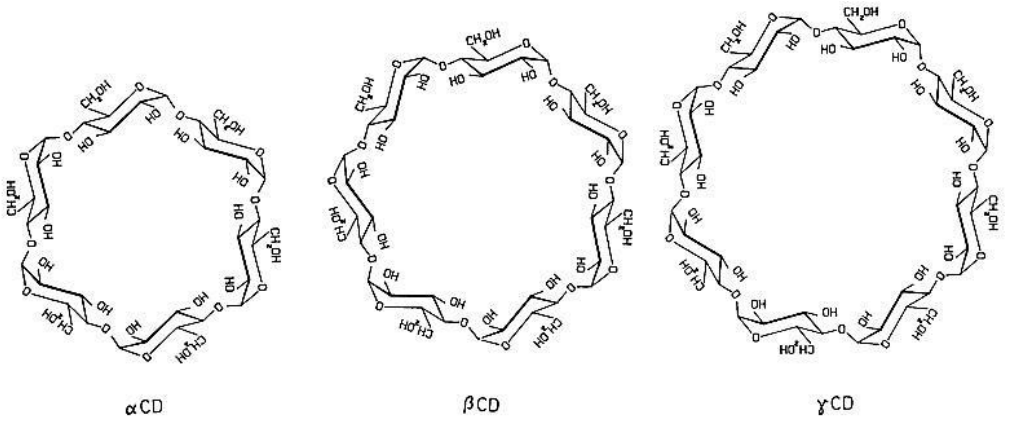


Figure 1.1: Structural representations of β-cyclodextrin, α-cyclodextrin, and γ cyclodextrin [16].

Due to the chair formation of the glucopyranose units, the cyclodextrin molecules are cone-shaped with secondary hydroxyl groups extending from the widest edge and the primary hydroxyl groups from the narrow edge as shown in Fig. 1.2 [18].

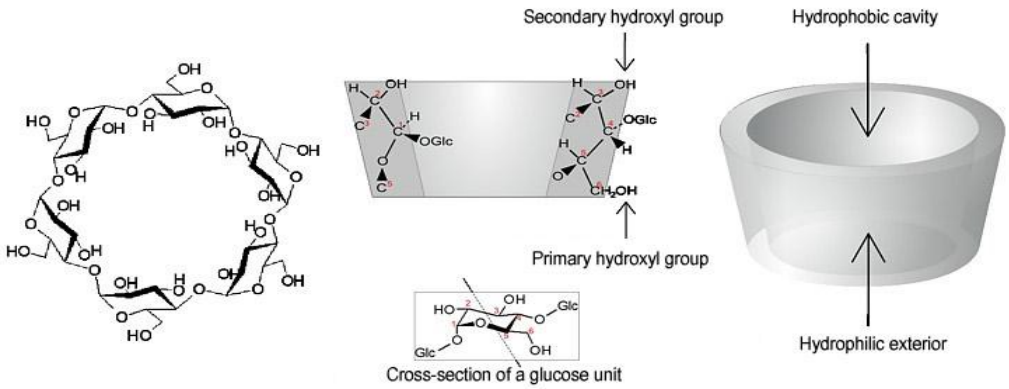


Figure 1.2: Molecular structure of β-cyclodextrin, cross-section of a cyclodextrin molecule showing the arrangement of a glucose unit and conical representation showing hydrophilic exterior and hydrophobic cavity [19].

Cyclodextrins are mainly used as a host/guest kind of inclusion as shown in Figure 1.3 [16].

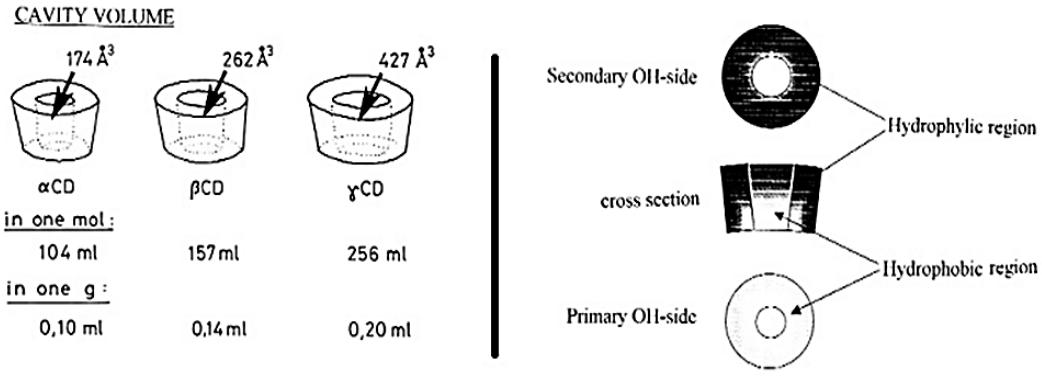


Figure 1.3: Dimensions and hydrophilic/ hydrophobic regions of the CyD molecules [16].

The solubility of cyclodextrins is very poor in organic solvents and this inhibits cyclodextrins from becoming effective complexing agents. It was discovered that chemical modification of 2-, 3-, and 6-hydroxyl could greatly increase solubility.

The 7-membered β-CyD is the least water soluble then the 6-membered and the 8-membered γ-CyD is most soluble (220 mg/mL) [16]. Solubility of the three cyclodextrins (α-, β-, and γ-CyD) is shown in Table 1.1.

Table 1.1: Solubility of the three cyclodextrins α-, β-, and γ-CyD [17].

Cyclodextrin	MW	Solubility in water (mg/ml)
α-Cyclodextrin	972	145
β-Cyclodextrin	1135	18.5
γ-Cyclodextrin	1297	232

1.3 Applications of Cyclodextrin

Cyclodextrins are useful functional excipients that have enjoyed widespread attention and use. The basis of this popularity from the pharmaceutical point of view is the ability of these materials to interact with drugs that are poorly soluble in water and with candidate drugs, which results in an increase in their apparent water solubility. Cyclodextrins have a wide range of applications in different areas of drug administration and the pharmaceutical industry due to their capacity for complexation and other versatile characteristics [21]. Cavity size is the major determinant as to which cyclodextrin is used in complexation. “Fit” is critical to achieving good incorporation of cyclodextrins. The α-Cyclodextrins have small cavities that are not capable of accepting many molecules. γ- Cyclodextrins have much larger cavities than many molecules to be incorporated, and cyclodextrin hydrophobic charges cannot effectively interact to facilitate complexation. The cavity diameter of β-cyclodextrins has been found to be the most appropriate size for hormones, vitamins, and other compounds frequently used in tissue and cell culture applications. For this reason, β-cyclodextrin is most commonly used as a complexing agent. Hydrophobic molecules are incorporated into the cavity of cyclodextrins by displacing water. This reaction is favored by the repulsion of the molecule by water. This effectively encapsulates the molecule of interest within the cyclodextrin, rendering the molecule water-soluble. When the water-soluble complex is diluted in a much larger volume of aqueous solvent, the

process is reversed, thereby releasing the molecule of interest into the solution [20].

Both the parent cyclodextrins and their derivatives have been used in dispersed vehicle systems such as emulsions, microcapsules, microspheres, nanospheres, nanocapsules, liposomes and niosomes. Cyclodextrins have been used to increase drug loading of polymeric microspheres or to increase drug availability from dispersed systems. Novel surface active cyclodextrin derivatives have also been synthesized and used as drug delivery systems [21]. Because of the diverse types of application of cyclodextrins, several types of medicinal products may contain cyclodextrins. They are used for example in tablets, aqueous parenteral solutions, nasal sprays and eye drop solutions [22].

Many metabolically important compounds, such as lipid-soluble vitamins and hormones, have very low solubility in aqueous solutions. Various techniques have been used to solubilize these compounds in tissue culture, cell culture, or other water-based applications. A frequently used approach is to use cyclodextrin as a “carrier” molecule to facilitate the dissolution of these compounds [20]. Cyclodextrins can be used to improve the drug delivery from almost any type of drug formulations. Cyclodextrins are not only well-known solubilizers, but constitute very powerful tool as permeation enhancers. There are a number of exciting possibilities for future applications of cyclodextrins, including new uses for existing derivatives, as well as the development of new derivatives. Cyclodextrins

having properties of increasing solubility, bioavailability, stability etc. may solve various problem associated with drug delivery through the complexation [21].

A series of products containing CyD, or technologies that use CyD is widely known in the food, cosmetic and toiletries, chemical products and technologies, biotechnology and pharmaceutical industries. For the next decade, significant new applications are expected of the use of CyD in environmental protection, biotechnology and in various industries, like the textile industry [16].

1.4 Citric Acid

Citric acid (2-hydroxy 2, 3-propanetricarboxylic acid) is a tricarboxylic acid with molecular formula $C_6H_8O_7$ [28]. It is an intermediate product of plant and animal metabolism and the most important organic acid produced in very large quantities by fermentation with an estimated annual production of about 1.4 million tons [29]. The 3D structure of citric acid is shown in figure 1.4.

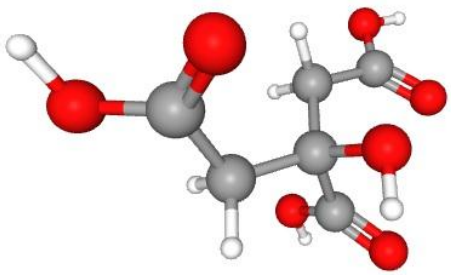


Figure 1.4: The 3D molecular structure of citric acid

Citric acid is a triprotic acid, having three pKa values 3.13, 4.76 and 6.40. However, a study showed that the deprotonation of the hydroxyl group in citric acid in a strongly basic solutions showed a pKa of 13.0 as shown in the following scheme.

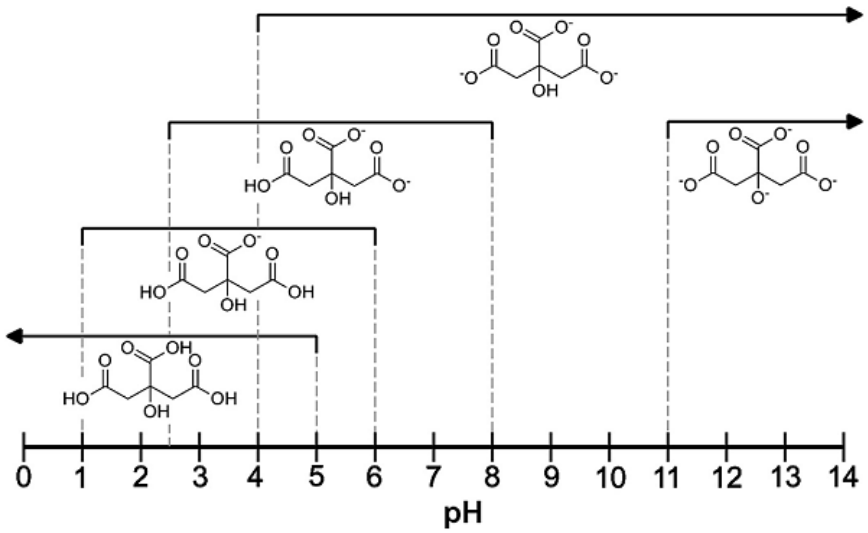


Figure 1.5: The unionized acid and related citrates exist in aqueous solutions in specific pH ranges (25^{o}C, 0.1 M) [28].

1.5 Toxic Metals

Heavy metals are those with high atomic weight [30] and have relatively high density, moreover are toxic at minimum concentrations. A large number of elements fall into this category, but the ones listed in Table 1.2 are those of relevance in the environmental context [31]. Examples on heavy metals are Copper, Silver, Zinc, Cadmium, Gold, Mercury, Lead, Chromium, Iron, Nickel, Tin, Arsenic, Selenium, Molybdenum, Cobalt, Manganese, and Aluminum [32]. Heavy metals enter the environment by natural sources such as natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents, pest or disease

control agents applied to plants, air pollution fallout, and others [33]. They showed a serious threats to the human water sources [32]. Mainly, they are toxic as shown in the following table.

Table 1.2: The maximum contaminant level (MCL) standards for the most hazardous heavy metals [34].

Heavy metal	Toxicities	MCL(mg/L)	Heavy metal	Toxicities	MCL(mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.05	Nikel	asthma, coughing, human carcinogen	0.20
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01	Zinc	Depression, lethargy, neurological signs and nervous system	0.80
Chromium	Headache, diarrhea, nausea, vomiting, carcinogen	0.05	Lead	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.006
Copper	Liver damage, Wilson disease, insomnia Dermatitis, nausea, chronic	0.25	Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system and nervous system	0.00003

Heavy metal contamination of water by industry is considered a major health concern [9,10]. Industry's waste contains several organic and inorganic materials. Among these materials are heavy metals, as mentioned above are very toxic and may be some of them are carcinogen. The most toxic metals are lead (Pb), zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni) and mercury (Hg) [35]. Heavy metals are easily absorbed by fish and vegetables due to their high solubility in the aquatic environments [10]. They can be absorbed and accumulated in human body and cause serious health effects like cancer, organ damage, nervous system damage, and in extreme cases, death. Also it reduces growth and development [32]. The heavy metals present in wastewater affect the bones, kidneys, liver, lungs and brain when Entered the body

through a number of path ways. When toxic metals are exposed to natural eco-system, metal ions such as lead, chromium, mercury and cadmium accumulate in body through direct intake or from food chains [36]. Heavy metals like arsenic, copper, cadmium, chromium, nickel, zinc, lead, and mercury are major pollutants of freshwater reservoirs because of their toxic, non-biodegradable, and persistent nature [10]. The salts of the heavy metals beryllium, cadmium, chromium, copper, lead, mercury, nickel and zinc are all of high eco-toxicity [37].

Many food elements are essential for human life at low concentration; however, some could be toxic at high concentrations. Some elements such as mercury, cadmium and lead are toxic even at very low concentration when adsorbed by creatures bodies over a long period [38].

There are five major sources of heavy metals in aquatic systems; Geological weathering, Industrial processing, the use of metals and metal compounds, Burning of fossil fuels, and Leaching of metals from garbage and solid waste dumps [39].

Some of the conditions for the discharge of effluent from industry to rivers and streams (UK) for some metals such as arsenic, cadmium, chromium, copper, lead, nickel, zinc, individually or in total is 1 mg/l are shown in Table 1.3. [37].

Table 1.3: Drinking water contaminants, their MCL, and toxicities [10]

Contaminants	MCL[a] or TT[b] [mg L^{-1}]	Potential health effects from long-term exposure above the MCL (unless specified as short term)
Cd	0.005	Kidney damage
Cr(total)	0.1	Allergic dermatitis
Cu	TT action level = 1.3	Short-term exposure: Gastrointestinal distress; long-term exposure: liver or kidney damage
As	0.010	Skin damage or problems with circulatory systems and may have increased risk of getting cancer
Pb	TT action level = 0.015	Infants and children: delays in physical or mental development, children could show slight deficits in attention span and learning abilities; adults: kidney problems; high blood pressure
Ni	0.20	Dermatitis, nausea, chronic asthma, coughing, human carcinogen
Zn	0.80	Depression, lethargy, neurological signs, and increased thirst
Hg	0.00003	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system

[a]Maximum contaminant level (MCL): the highest level of a contaminant that is allowed in drinking water; MCLs are enforceable standards; [b]treatment technique (TT): a required process intended to reduce the level of a contaminant in drinking water.

1.5.1 Lead (Pb)

Lead is a naturally occurring bluish-gray metal available in small amounts in the Earth's crust [40]. Lead from Group IV can form two and four valence compounds. Two of the four outer electrons can behave as inert when the atoms are bivalent. The nitrate and sulphate of bivalent lead (plumbous) are ionic. Some tetravalent lead compounds such as the hydrides and chloride are unstable, e.g. [35]:

$$PbCl_4 + 2H_2O \text{ -----> } PbO_2 + 4HCl$$

Lead has a number of important applications in the present day, like it is used in acid batteries and as a gasoline additives, in electrical and electronic applications such TV tubes Also it is used as shield form the X-ray and γ-radiation [41].

Lead is considered as one of the most abundant heavy metals and its toxicity cause environmental and health problems because of its stability in contaminated site and complexity of mechanism in biological toxicity, particularly dangerous for children leading to mental retardation when exist with abnormal concentration in body fluid [40]. Lead is toxic to human it causes damage to kidney, liver, reproductive system and brain [35].

1.6 Wastewater

Contaminated water (wastewater) is water with physical, chemical and biological properties that was changed due to the entry of some substances which makes it unsafe for some usage such as drinking or cooking. Sewage is a term used for dark water that is obtained from a sewerage system [7]. Wastewater sources include homes, businesses and industries. Rain water can enter the wastewater system and add to the volume of wastewater in sewage system [42]. Domestic sewage usually comes from kitchens, bathroom, etc. Municipal sewage, usually contains both domestic and industrial wastewater. The contents of the sewage water might vary from place to another depending upon the type of industries [43].

Wastewater combinations are summarized in the following figure [44].

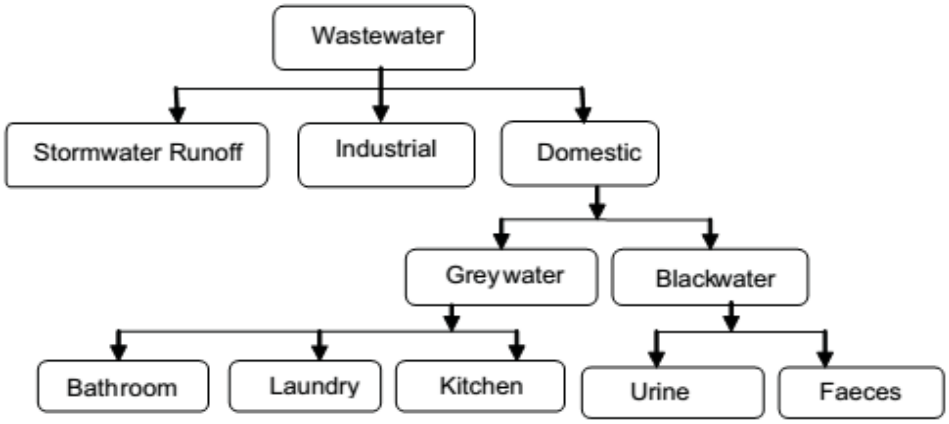


Figure 1.6: Types of Wastewater [7]

Discharge of domestic or industrial wastewater, or in a diffused form, as in the application of fertilizers or pesticides onto the soil. Both contribute to the entry of compounds into the water, thus affecting its quality [42]. Industrial wastewater mainly contains toxic organic compounds chemicals and metal ions [45].

The important characteristics of sewage are temperature, pH, color and odor, solids, nitrogen and phosphorus, chlorides, organic material, and toxic metals and compounds. Wastewaters from industries can form important component of sewage in both volume and composition [43].

Wastewater should be treated to prevent pollution problems in receiving containers. Waste discharges can be diveded into two types: organic wastes which are carbon based and inorganic wastes such as metals, minerals, salts, acids and bases [46]. Treatment of wastewater

becomes a necessity when these materials exceed a certain level assigned by responsible organizations [7].

1.7 Wastewater in Palestine

Palestinian territories is one of the most water-poor territories of the Middle East which is related to natural and artificial constraints. The gap between water supply and water needs is growing to a critical level. The increased number of people in the region and rapid increase in the industry has caused an increased imbalance between water supply and demand. So, wastewater treatment and purification could be an alternative source can help bridge the imbalance. Wastewater treatment is seen as one of the most promising solutions for this issue [47].

The total volume of wastewater generated for year 2015 by the Palestinian cities is summarized in the figure below [48].

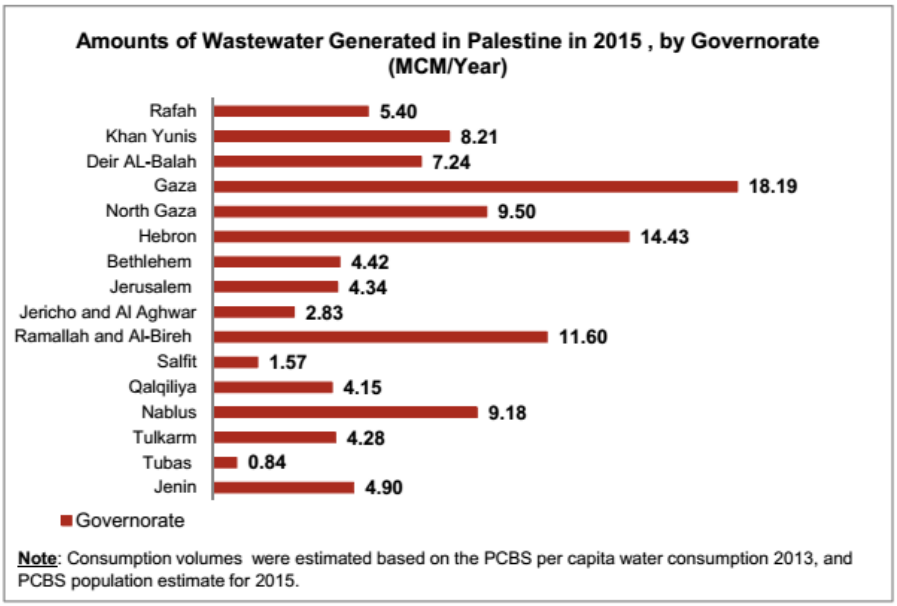


Figure 1.7: Estimated volume of wastewater generated in WB&G governorates in 2015

The Israeli factories and industrial zones located in West Bank at the border with the Israeli territories are considered as the major contributor to water pollution in the Palestinian area. The generated wastewater from the industrial zones flows towards the Palestinian lands located at the foothills of these industrial zones, the generated solid waste is dumped near and into the Palestinian lands without any treatment. Aluminum, leather tanning, textile-dyeing, batteries, fiberglass, plastics and other chemicals are the major Israeli industries. The wastes contains toxic metals such as aluminum, chromium, lead, zinc and nickel. These practices cause in damaging the water resource and soil, as well as polluting the air and affecting human health [48]. Therefor developing a method for removing these toxic materials for the wastewater generated by the Palestinian and Israeli becomes demand.

1.8 Aim of the work

1.8.1 General Objectives

1. Develop an approach to synthesize cross-linked β-cyclodextrin with citric acid, then using new polymer as an adsorbent to remove toxic metals (Pb^{2+}, Fe^{3+}, Cr^{3+}) from wastewater.

2. To study the effect of various factors such as pH, temperature, amount of adsorbent, concentration and contact time on the adsorption efficiency of cross-linked β-cyclodextrin.

3. To study the adsorption behaviors of the prepared polymer with (Pb^{2+}) solutions.

4. To determine if cross-linked β-cyclodextrin can be used to clean up toxic metals that polluted wastewater.

Chapter Two

Experimental

2.1 Materials and Methods

All reagents, solvents and chemicals used in this work were of analytical grade and used without further purification. The β-cyclodextrin was supplied by Sigma-Aldrich having purity ≥ 97%. Citric acid was from Sigma-Aldrich with purity ≥ 99.5%. Lead nitrate, iron (III) chloride, and chromic chloride hexahydrate were used to prepare stock solutions with 1000 ppm concentration. Deionized water was used to prepare stock solutions. Diluted solutions of (0.1M) HCl and (0.1M) NaOH were used for pH adjustment to the desired value.

The following instruments were used to accomplish this research: Water bath with a shaker Digital Speed Control, pH meter, FT-IR Spectrometer.

The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with the Smart Split Peatm 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 surface morphology of the cellulose polymer and derivatives were examined using scanning electron microscopy (SEM) (S-4800; Hitachi, Tokyo, Japan) at an acceleration

voltage of 3.0 kV after sputter coating the sample with gold (Cressington Sputter Coater; Ted Pella, Inc., Redding, CA, USA). Flame Atomic Absorption Spectrometer iCE 3xxx C113500021 v1.30, Shaking Water Bath (Daihan Labtech, 20 to 250 rpm Digital Speed Control).

2.2 Synthesis of cross-linked β-cyclodextrin (co-β-CyDe-CA)

2.2.1 Synthesis of polymer (A)

A solution of citric acid and β-cyclodextrin in 1:1 ratio (1.0 g each) was prepared in deionized water (10.0 mL). The mixture was stirred until a clear solution was obtained. The solution was placed in an oven at 110 °C until water evaporate completely. After that, the oven temperature was raised to 170 °C, and the mixture was kept under these conditions for two hours. The mixture was removed from oven, cooled down to room temperature and grinded.

2.2.2 Synthesis of polymer (B)

The same procedure used for the preparation of polymer A was followed, the only difference is quantity of citric acid was increased to 3.0 g, and β-cyclodextrin still 1.0 g (3:1 ratio).

The prepared cross-linked polymers were analyzed by FT-IR spectroscopy to confirm the structure of the target materials.

2.2.3 Water solubility

Polymers solubility in water was examined. A sample of each polymer with known weight (1.0 g) was suspended in water (100 ml) and stirred for about 10 hours, and then collected by suction filtration, dried in an oven at 110^{o}C, and weighed. Negligible reduction in the weight was noticed.

2.3 Preparation of metals solutions

A stock solution with a concentration of 100 mg/L of the three heavy metal ions (Pb^{2+}, Fe^{3+}, Cr^{3+}) were prepared; then from stock solution various diluted solutions were prepared according to the following formula:

The needed weight = volume (lit) X the needed conc. (mg/lit) X (1 / mass of cation) (mol/g) X (mass of salt /1) (g/mol)

2.3.1 Preparation of a 100 mg/L Pb^{2+} stock solutions

A 0.8000 g of Lead nitrate was added to a 500 mL volumetric flask and diluted up to the mark by addition of deionized water. Different concentration 5, 10, 20 and 50 mg/L were then prepared form the stock solution by dilution.

2.3.2 Preparation of 100 mg/L Fe^{3+} stock solutions

A 1.4500 g of Iron (III) chloride was added to a 500 mL volumetric flask and diluted up to the mark by addition of deionized water. Different

concentration 5, 10, 20 and 50 mg/L were prepared form the stock solution by dilution.

2.3.3 Preparation of 100 mg/L Cr^{3+} stock solutions

A 2.5600 g of chromic chloride hexahydrate was added to a 500 mL volumetric flask and diluted up to the mark by addition of deionized water. Different concentration; 5, 10, 20 and 50 mg/L were prepared by dilution.

2.4 Extraction of toxic metals

A batch extraction process was used, whereas known amount of polymer (co-β-CyDe-CA) was added to the metal ions solution with known concentration in a bottle, then the bottle was closed and shacked in the shaker apparatus at constant temperature and at a specific speed for certain period of time according to the factor which is under study. A sample of each mixture was withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis for residual metal ions concentrations by atomic absorption spectroscopy.

The proportion of metal adsorption (% Adsorption) is recognized as the ratio of disparity of the metal ions concentration before and after adsorption to the initial concentration of the metal ions in the aqueous solution and was calculated using the following equation [49]:

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

Where, C_o is the Initial metal ions concentration (mg/L) in the sample and C_e is the final metal ions concentration in the sample solution after treatment.

Under the experimental conditions, the adsorption capacity for each concentration of metal ions at equilibrium was determined by the following expression [50].

$$q_e\left(\frac{mg}{g}\right) = \left[\frac{C_i - C_e}{m}\right]V \qquad (2.2)$$

Where V is the volume of solution (in liters) and M is the mass of adsorbent (in grams) used.

2.4.1 Effect of pH on the removal efficiency of toxic metal ions

Effect of solution pH on adsorption was investigated in the range of 2.0-10. The pH was adjusted using roughly concentrations of 0.1M HCl and 0.1M NaOH. Samples of 0.1 g polymer were added to a 10 mL of metal ions solutions with concentration 50 mg/L. The mixtures were placed in thermstated water bath at 30℃ for 30 min. At the end of each time interval, an aliquot of each mixture was withdrawn with a syringe, filtered through a 0.45 μm syringe filter and subjected to analysis to determine residual metal ion concentrations by atomic absorption spectroscopy. The previous steps were repeated using polymer (B).

2.4.2 Effect of temperature on the metal ions removal

For studying the temperature effect on adsorption, a 0.10 g samples of polymer A was added to a 10 mL of metal ions solutions with concentration of 50 mg/L at pH around 9. Each mixture was placed in Shaking Water Bath (Daihan Labtech) at a desired temperature (the range was 25-40°C) for 30 min. At the end of each time interval of the specified temperature, an aliquot of each mixture was extracted with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis to determine residual metal ion concentrations. The concentration of residual metal ions was determined by atomic absorption spectroscopy. The previous steps were repeated using polymer (B).

2.4.3 Effect of polymer dose on the removal efficiency

The effect of polymer dose on the removal of metal ions was studied, in order to determine the optimum dose. Doses of 0.05, 0.10, 0.15 and 0.20 g of the polymer were added to the four vials that contains 10 mL of 50 mg/L metal ions solution of pH around 9. After that, a sample from each mixture withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis for residual metal ions concentrations. The mixtures were placed in Shaking Water Bath at constant temperature (25°C) for 30 min. The concentration of lead metal was determined by atomic absorption spectroscopy. Similar procedure was followed repeated using polymer B.

2.4.4 Optimization of contact time

The removal of metal ions by the prepared polymers was studied as a function of shaking time at 30^{o}C. Five samples of 10 mL of metal ions solution with concentration of (50 mg/L) adjusted at pH value of 9 were taken in five volumetric flasks and shaken with 0.1 g of polymer (A) that was added to each one. The solutions were shaken for different periods (5 min, 10 min, 15 min, 20 min, and 30 minutes). A portion of each mixture was withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis for residual metal ions concentrations. The concentration of metal ions was determined by atomic absorption spectroscopy. The same procedures were repeated using polymer (B).

2.4.5 Effect of initial concentration of metal ions

In order to determine the optimum initial concentration of ions, a 0.1 g of polymer (A) was added to a number of vials each contains a 10 mL of different concentrations of metal ions solution (10-50 mg/L), under optimized temperature (30^{o}C) and pH around 9 for 30 min. The concentration of residual metal ions was determined by atomic absorption spectroscopy. The previous steps were repeated using polymer B.

2.5 Kinetics of adsorption process

The removal of toxic metal ions was studied by adsorption technique using the prepared polymer (co-β-CyDe-CA). The method was arranged under the optimized condition of polymer dose, contact time, concentration

of metal ions, temperature and pH. Using atomic absorption spectroscopy, the concentration of metal ions was determined before and after adsorption. The data were provided into Langmuir and Freundlich adsorption isotherm equations.

Amount of 0.1 g of polymer was added to 10 mL of 50 mg/L of metal ions solution at pH 9.04. The mixture was placed in a water bath equipped with a shaker at a constant temperature of 30°C. The rate of adsorption was observed by studying the contact time up to 2 hours and matched to theoretical models. Pseudo first-order and second-order kinetic models were examined in this study using experimental data obtained for different periods of contact time. Parameters of Pseudo first and second order kinetic models, (K, Q_e and R^2) for metal ions adsorption on (co-β-CyDe-CA) were determined. The values of the calculated and experimental Q_e were compared.

2.6 Wastewater purification

A sample of sewage water collected form the sewage system (Palestine) was used in this study. The sample was subject to analysis by ICP-AES (the analysis was performed by the Water Center at An-Najah National University, Nablus, Palestine) to determine the metals content and their concentrations. Two 50.0 mL samples of the sewage water were placed in two Erlenmeyer flasks and their pH values were adjusted 6.3 and 8.3. To each sample was added 0.1 g of the cellulose amine polymer 2. The mixtures were shaken at room temperature for 30 min. A sample of each

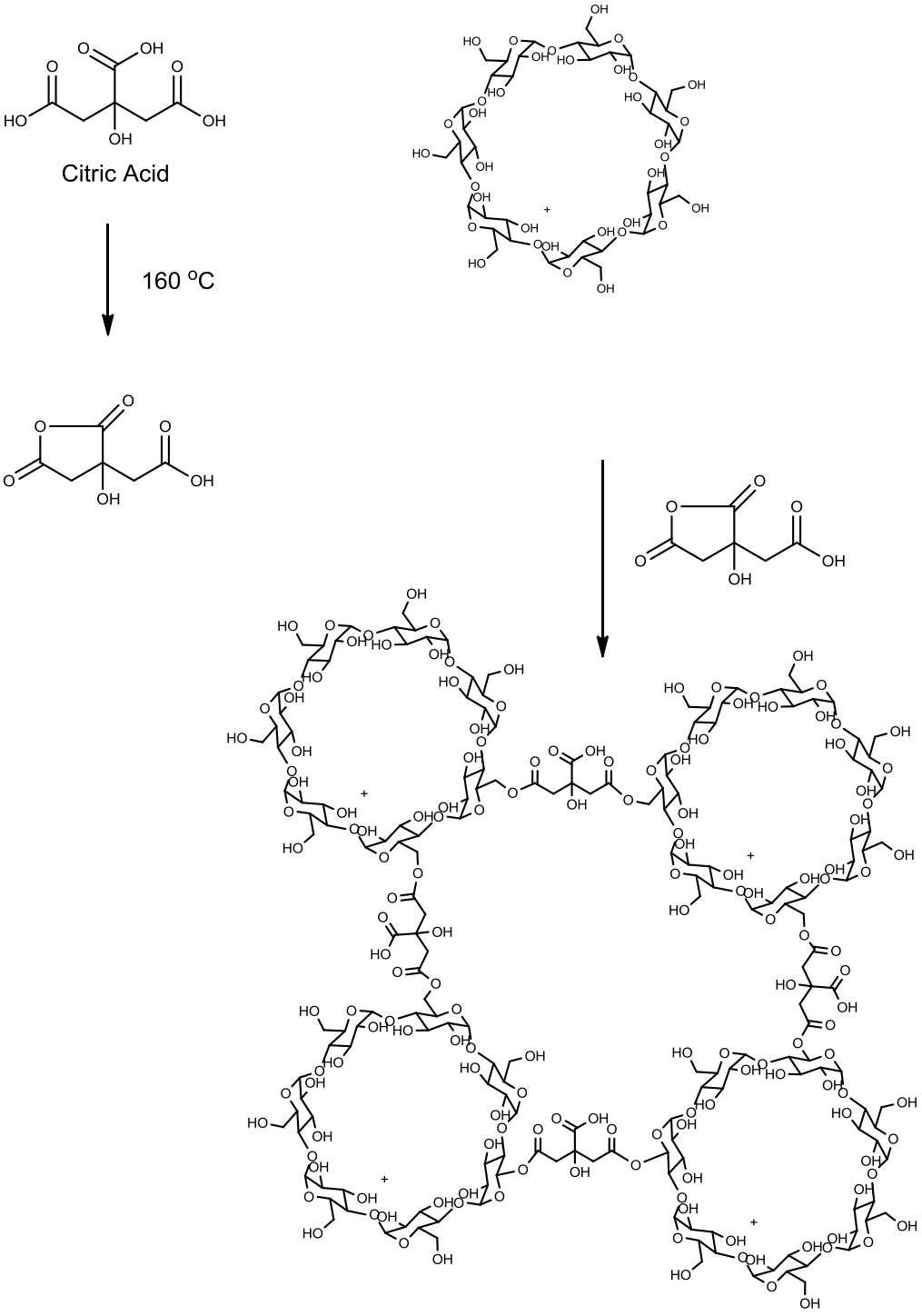
mixture was withdrawn with a syringe and pushed through a 0.45 μm syringe filter and subjected to analysis by ICP-AES for residual metal ions concentrations.

Chapter Three

Results and Discussion

3.1 Preparation of the co-polymer β-cyclodextrin-citric acid (co-β-CyDe-CA)

A solution of citric acid and cyclodextrin was prepared. water was then evaporated to dryness. Preparation of solution from the two chemicals was important in order to obtain an even distribution of chemical (a homogeneous mixture). The polymerization and crosslinking process were promoted by heating the mixture at 170 ^{o}C. As shown in scheme 3.1 at 170 ^{o}C the adjacent carboxyl groups in citric acid loses a water molecule and form anhydride. The anhydride very reactive functionality, it undergoes nucleophilic addition reaction with hydroxyl group of cyclodextrin to form an ester linkage.



Scheme 3.1: Stepwise reaction mechanism of (co-β-CyDe-CA) synthesis.

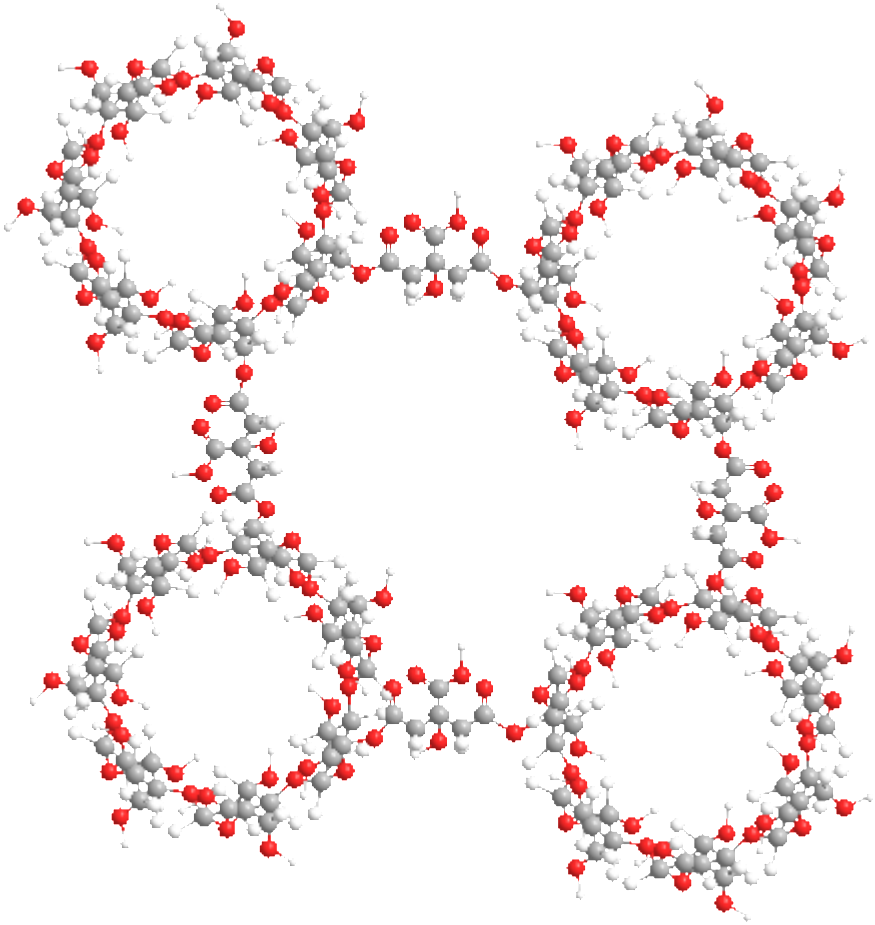


Figure 3.1: A 3D structure of (co-β-CyDe-CA)

3.2. FT-IR Characterization of the prepared polymer (co-β-CyDe-CA)

The products formed from the reaction between β-cyclodextrin polymers (A and B) were evaluated using FT-IR spectra. The FT-IR spectra of starting martials β-cyclodextrin and citric acid were also recorded. As shown in Figure 3.3, the FT-IR spectrum of citric acid shows two sharp peaks at about 1710 and 1746 cm^{-1} which could be attributed to the C=O stretching. The peak crossponding to C=O showed as strong broad in (co-β-CyDe-CA) polymer. The peak shape could be an indication of the formation a new carbonyl group beside the carbonyl of acid that is for an ester group. Furthermore, both β-CyD and (co-β-CyDe-CA) polymer show

an evidence of carbon in cyclic rings at 1027 and 1045 cm^{-1}. The FT-IR also show the presence of C–H stretching vibration absorption bands at 2929 cm^{-1} and 2942 cm^{-1} crossponding to β-CyD and (co-β-CyDe-CA) respectively. Also FTIR had shown the presence of the broad absorption band at 3285 cm^{-1} for citric acid, 3324 cm^{-1} for β-CyD, 3419 cm^{-1} for polymer (A) and 3397 cm^{-1} for polymer (B), assigned to O–H stretching. These evidences confirm the formation of an ester linkage between β-cyclodextrin and citric acid [27].

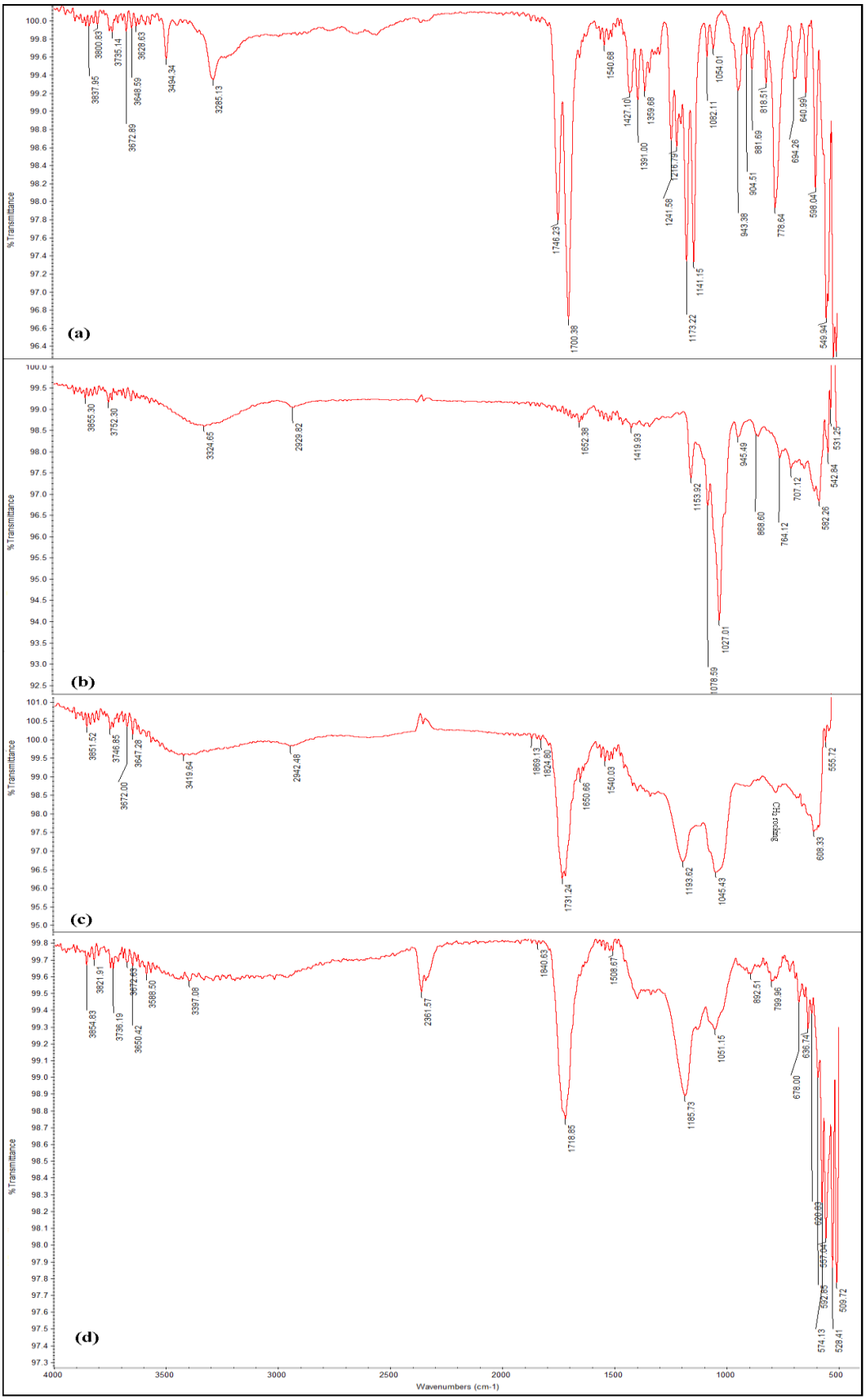


Figure 3.2: FT-IR spectra of (a) Citric acid (b) β-cyclodextrin (c) Polymer A (d) Polymer B

3.3 Surface analysis by SEM

The obtained SEM images of polymers A and B are shown in Figures 3.3 and 3.4. Polymer obtained from mixing 1:1 ratio of citric acid and β-cyclodextrin showed a solid surface with little number of holes. However, the one prepared form mixing 3:1 ratio by weight of citric acid and β-cyclodextrin showed high porosity, which could be related to high degree of crosslinking and more carboxyl groups.

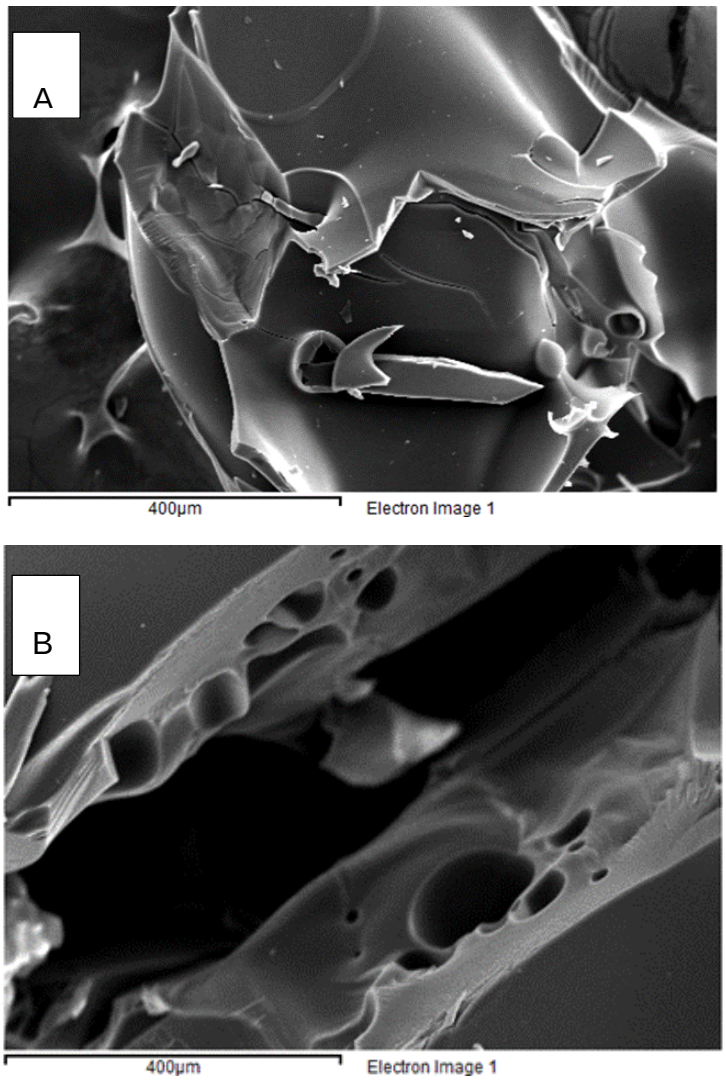


Figure 3.3: SEM images of polymer A at 500x (a) and 250x (b)

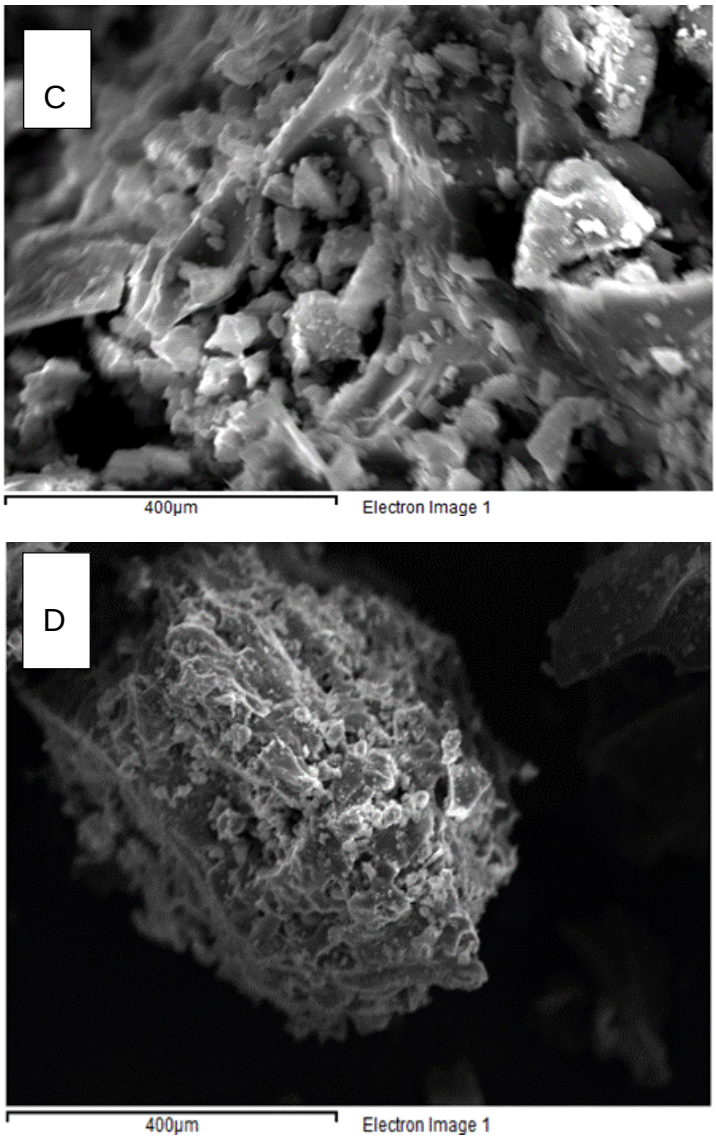


Figure 3.4: SEM images of polymer B at 500x (a) and 100x (b)

3.4 Effect of various parameters on adsorption efficiency

The objective of this study is to examine the efficiency of new ploymer as an adsorbent for toxic metals from wastewater. The adsorption behavior 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 Temperature effect on adsorption efficiency

The effect of temperature on the extraction of lead ions by (co-β-CyDe-CA) was studied at temperature range from 25°C to 40°C as shown in Figure 3.5 for polymer (A). The figure shows that the removal percentage of lead ions increases slightly by raising the temperature, it reaches the maximum at around 30°C which was 83%, and then decreasing above this temperature. This indicates that the removal of lead ions by polymer (A) is an exothermic process.

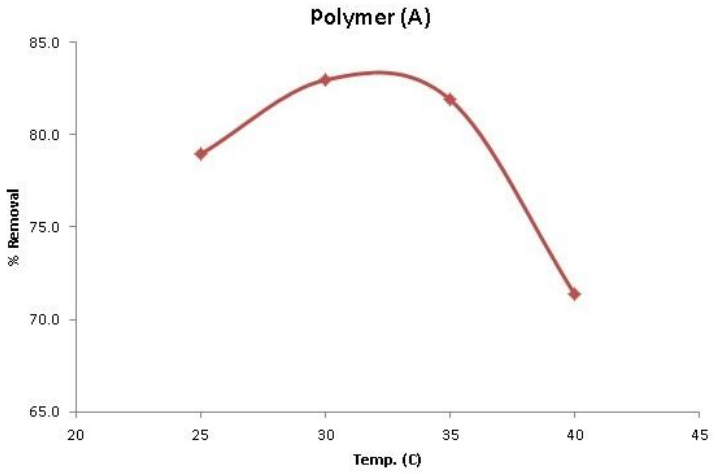


Figure 3.5: Temperature effect on the removal efficiency of lead ions for polymer (A). (c_o= 50 mg/L, time= 30 min., adsorbent dose= 0.1 g, solution volume = 10 mL, pH neutral)

Figure 3.6 represents the impact of temperature on the removal percentage of lead ions for polymer B.

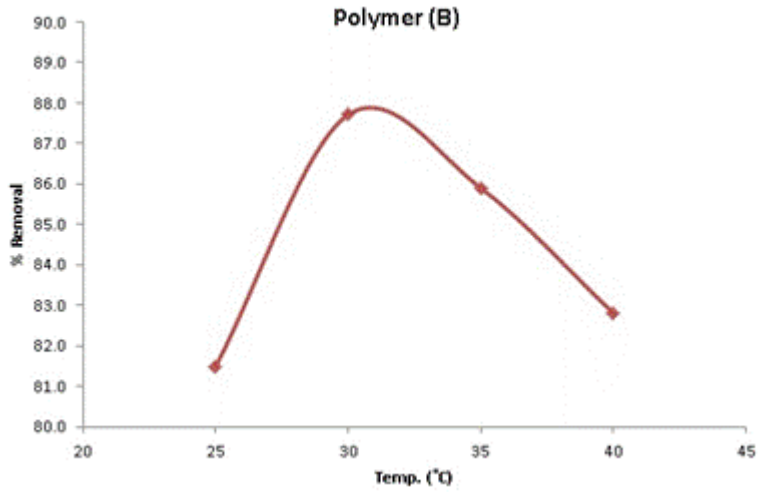


Figure 3.6: Temperature effect on the removal efficiency of lead ions for polymer (B). (c_o= 50 mg/L, time= 30 min., adsorbent dose= 0.1 g, sol. Volume= 10 mL, pH =neutral)

The optimum temperature at which the high removal was achieved is 30^{o}C for both polymers A and B. The results are in Table 3.1 and Table 3.2.

Table 3.1: Temperature effect on the removal efficiency of lead ions for polymer (A). (c_o= 50 mg/L, time= 30 min., adsorbent dose= 0.1 g, sol. Volume= 10 mL)

Temp. ˚C	% Removal
25	78.9
30	83.0
35	81.9
40	71.4

Table 3.2: Temperature effect on the removal efficiency of lead ions for polymer (B). (c_o= 50 mg/L, time= 30 min., adsorbent dose= 0.1 g, solution volume= 10 mL)

Temp. ˚C	% Removal
25	81.5
30	87.7
35	85.9
40	82.8

3.4.2 Effect of polymer dose on the removal efficiency of lead ions

The impact of the dose of polymers A and B on the removal of lead ions from an aqueous solution was studied. Initial concentration of lead ions solution was kept at 50.0 mg/L and solution volume was 10.0 mL, pH was adjusted to 9 and temperature was preserved at 30 ^{o}C. The results were summarized in Table 3.3 and were represented in Figure 3.7 for polymer A, and in Table 3.4 and Figure 3.8 for polymer B.

Table 3.3: Effect of polymer dose on the adsorption efficiency of lead ions for polymer (A), (c_o= 50 mg/L, time= 30 min., Temp.= 30^{o}C, sol. Volume= 10 mL)

sample	wt. of dose (g)	% of removal
1	0.05	70.4
2	0.10	71.4
3	0.15	71.0
4	0.20	70.7

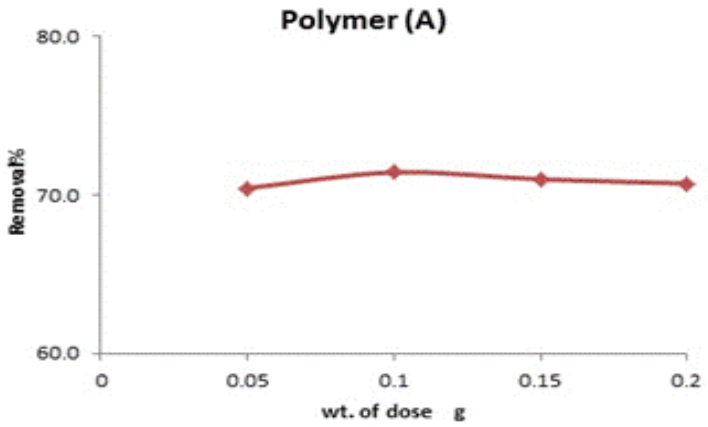


Figure 3.7: Effect of polymer dose on the removal efficiency of lead ions for polymer (A), (c_o= 50 mg/L, time= 30 min., Temp.= 30 ^oC, solution volume= 10 mL).

Table 3.4: Effect of polymer dose on the removal efficiency of lead ions for polymer (B), (c_o= 50 mg/L, time= 30 min., Temp.= 30^oC, sol. Volume= 10 mL)

sample	wt. of dose (g)	% of removal
1	0.05	80.4
2	0.10	80.0
3	0.15	80.6
4	0.20	78.9

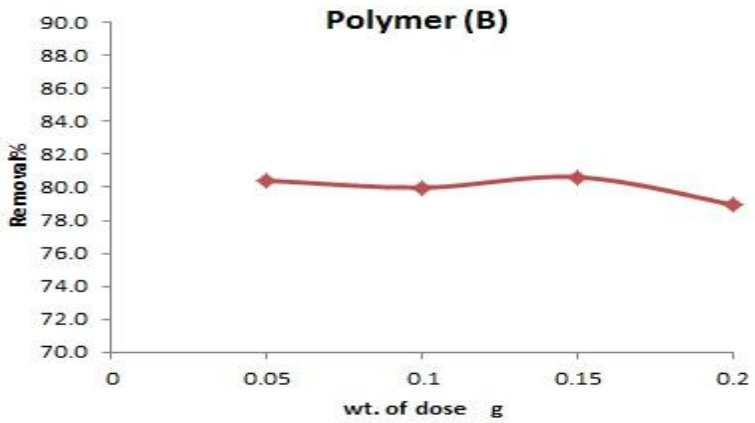


Figure 3.8: Effect of polymer dose on the removal efficiency of lead ions for polymer (B), (c_o= 50 mg/L, time= 30 min., Temp.= 30^oC, sol. Volume= 10 mL)

The results for both polymers demonstrate that removal of lead (II) by the two polymers didn't show dependence on adsorbent dose. The adsorption efficiency was about 71% for polymer A and about 80% for polymer B. The equilibrium stage was reached with 0.1 g of adsorbent dose for both polymers A and B. This could be due to the limited number of the active sites and the establishment of equilibrium in the concentration of Pb(II) between adsorbent and solution [53].

3.4.3 Optimization of contact time

The best and most effective contact time to achieve the maximum removal of lead ions from its aqueous solution by the prepared polymers was determined. The results are shown in Table 3.5 and demonstrated in Figure 3.9 for polymer A. The results that related to polymer B are shown in Table 3.6 and Figure 3.10.

Table 3.5: Effect of contact time on the removal efficiency of lead ions for polymer (A), (c_o= 50 mg/L, time= 30 min., Temp.= 30^{o}C, sol. Volume = 10 mL)

sample	time (min.)	% of removal
1	5	79.0
2	10	74.7
3	15	71.5
4	20	77.3
5	30	80.8

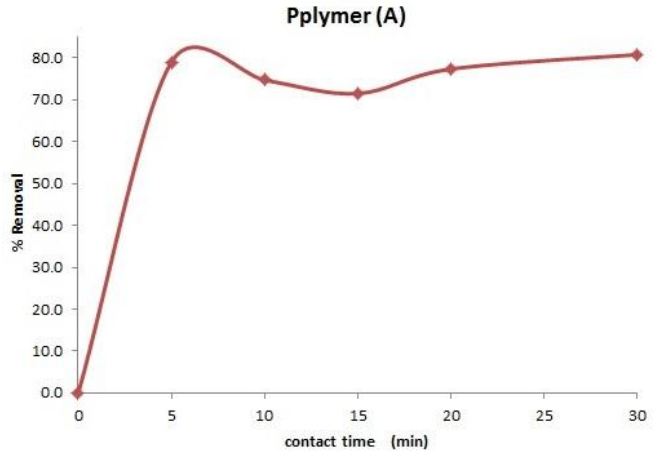


Figure 3.9: Effect of contact time on the adsorption efficiency of lead ions by polymer A, (c_o= 50 mg/L, time= 30 min., Temp.= 30^{o}C, sol. Volume = 10 mL)

Table 3.6: Effect of contact time on the adsorption efficiency of lead ions by polymer B, (c_o= 50 mg/L, time= 30 min., Temp.= 30^{o}C, sol. Volume = 10 mL)

sample	time (min.)	% of removal
1	5	82.8
2	10	83.1
3	15	83.6
4	20	81.9
5	30	83.3

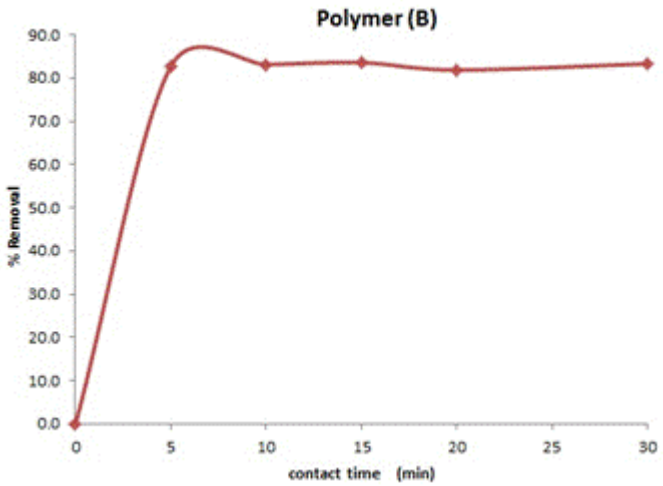


Figure 3.10: Effect of contact time on the removal efficiency of lead ions for polymer (B), (c_o= 50 mg/L, time= 30 min., Temp.= 30^{o}C, sol. Volume = 10 mL)

The above results for polymers A and B show a fast rate of adsorption that occurred in the first 5 minutes and then it becomes nearly insignificant constant, which could be due to the occupation of active sites.

The adsorption sites are high at the start due to the large availability of active sites on the adsorbent surface. At the beginning of the adsorption process all reactive sites are vacant and therefore the degree of removal is high [49]. After the initial rapid absorption, the removal rate almost reaching a constant value; with average removal percentage of 76% for polymer A and 83% for polymer B.

3.4.4 Effect of Pb(II) initial concentration on the adsorption efficiency

In order to determine the optimum concentration, 0.1 g of the prepared polymers was added to several vials each contain 10.0 mL of various concentrations of lead ions solution ranging from 10 to 50 mg/L, under optimized temperature 30^{o}C and pH around 9 for 30 min. The concentration of residual lead ions was specified by atomic absorption spectroscopy. The results are presented in Table 3.7 and demonstrated in Figure 3.11 for polymer A. The results that related to polymer B are shown in Table 3.8 and Figure 3.12. The data and figures show that, removal of lead ions was high at lower concentration and as concentration increases the amount of lead ions removed was decreased.

Table 3.7: Effect of lead concentration on the removal efficiency of polymer (A), (pH= 8.9, time= 30 min., Temp.= 30°C, sol. Volume = 10 mL)

conc. of lead (ppm)	% of removal
10	87.9
20	82.7
30	77.6
40	73.4
50	71.4

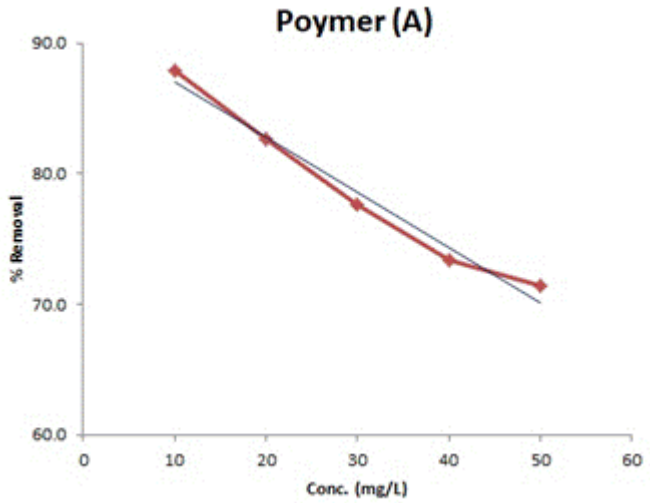


Figure 3.11: Effect of lead concentration on the removal efficiency of polymer (A), (pH= 8.9, time= 30 min., Temp.= 30°C, sol. Volume = 10 mL)

Table 3.8: Effect of lead concentration on the removal efficiency of polymer (B), (pH= 8.8, time= 30 min., Temp = 30°C, solution volume = 10 mL)

conc. of lead (ppm)	% of removal
10	90.9
20	87.7
30	84.6
40	83.1
50	82.9

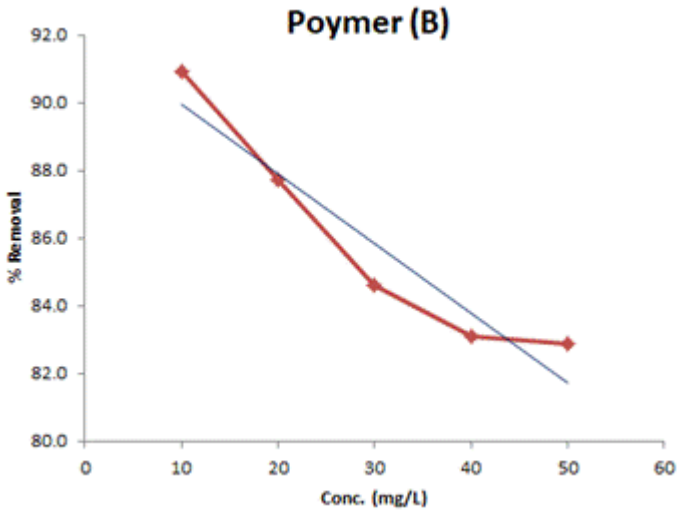


Figure 3.12: Effect of lead concentration on the removal efficiency of polymer (B), (pH= 8.8, time= 30 min., Temp.= 30^{o}C, sol. Volume = 10 mL)

At low concentration, the available sites are high compared to the initial number of lead ions, but at high concentrations of lead ions, the available sites are few compared to the initial number of lead ions [54]. Percentage removal of lead ions lowered from 88% to 71% for polymer (A) and from 91% to 83% for polymer (B).

Regarding polymer A; amount of lead ions absorbed increased from 0.88 to 3.57 mg/g by increasing the lead ions concentration from 10.0 to 50.0 mg/L as shown in Figure 3.13. While for polymer (B); it was from 0.91 to 4.15 mg/g with increasing lead ions concentration from 10 to 50 mg/L as shown in Figure 3.14. When all spots are taken by lead ions, the absorption becomes nearly steady whatever concentration of lead ions is increased.

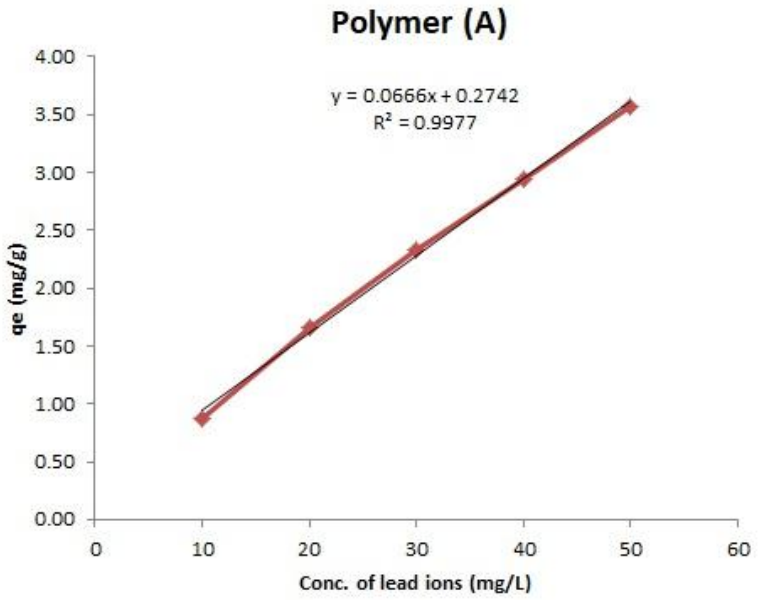


Figure 3.13: Effect of lead ions conc. on absorption capacity for polymer (A). (Temp.= 30°C, time= 30 min., pH= 8.9, dose= 0.1 g, Volume= 10 mL).

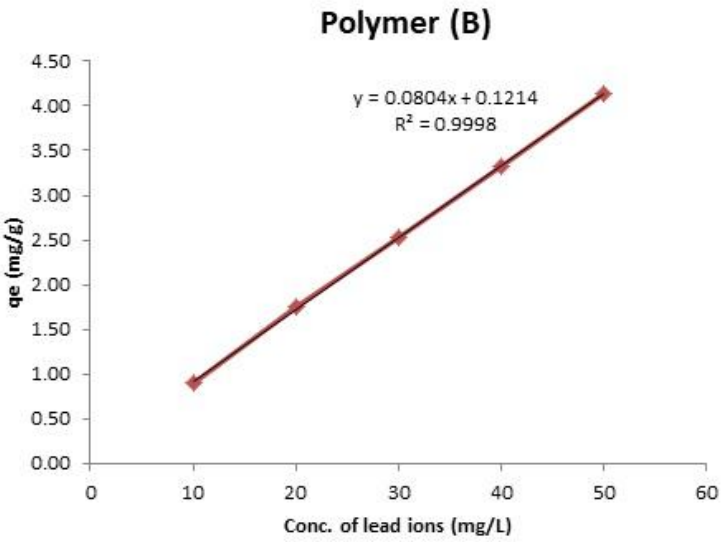


Figure 3.14: Effect of lead ions conc. on absorption capacity for polymer (B). (Temp.= 30°C, time= 30 min., pH= 8.9, dose= 0.1 g, Volume= 10 mL).

3.4.5 Effect of pH

The effect of pH value on adsorption efficiency of polymers A and B was evaluated. The pH value is crucial especially for adsorbents with functional groups that might protonated or deprotonated readily by varying

the pH value [51]. To study the impact of pH value on the adsorption capability of (co-β-CyDe-CA) polymers, the experiments were done in solutions with various pH. Figure 3.15 shows the effect of pH on the removal of lead ions from aqueous solutions by (co-β-CyDe-CA).

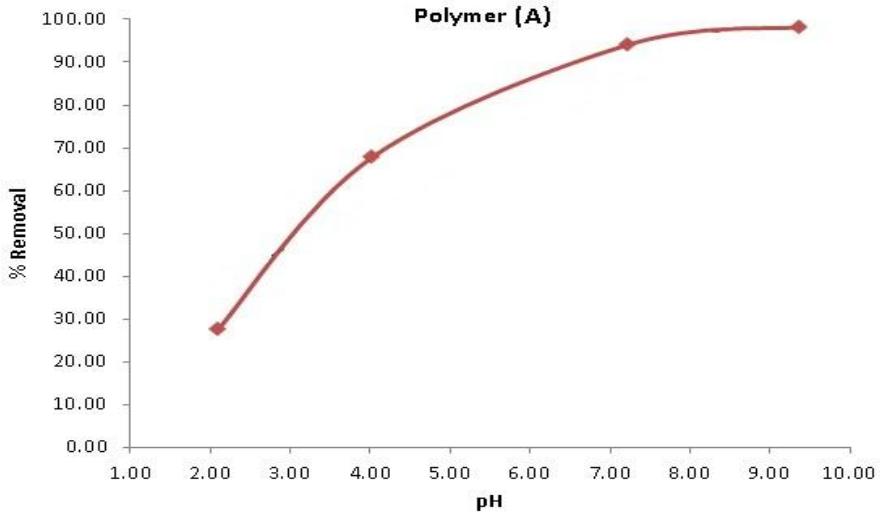


Figure 3.15: pH impact on lead ions removal. (C_o= 50 mg/L, time = 30 min., T = 30^{O}C, polymer (A) dose = 0.1 g, sol. Volume = 10 mL)

For polymer (A) results show that the rate of lead ions removal increase with pH. The removal percentage of lead ions reached its maximum 98.2 at pH 9.38 as shown in Table 3.9. Lower removal ability occurs at lower pH, which may be due to the existence of the carboxyl group [52].

Table 3.9: Effect of pH on the lead removal efficiency for polymer (A)

pH	[Pb^{2+}] mg/L	% Pb^{2+} Removal
2.11	38.08	27.8
4.03	16.06	67.9
7.23	2.94	94.1
9.38	0.90	98.2

Similar trend has been explored for polymer B as shown in Figure 3.16, where the removal percentage of lead ions reached its maximum removal 98.6 at pH 6.36 as shown in Table 3.10. Lower removal ability occurs at lower pH and no significant changes have been detected on the removal percentage above pH of 6.36.

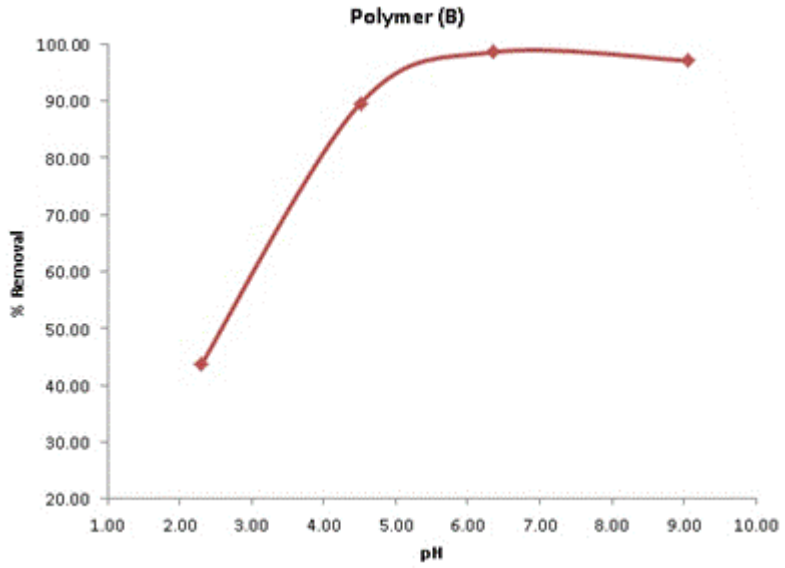


Figure 3.16: pH impact on lead ions removal by polymer B, dose = 0.1 g, volume = 10 mL, C_o= 50 mg/L, time = 30 min., T = 30^{O}C.

Table 3.10: Effect of pH on the lead removal efficiency for polymer (B)

pH	[Pb^{2+}] mg/L	% Pb^{2+} Removal
2.30	28.18	43.6
4.51	5.21	89.6
6.36	0.69	98.6
9.05	1.45	97.1

This behavior for the two polymers can be explained on the basis that citric acid is considered as a diprotic acid (a carboxyl group consumed in forming the polymer) having two dissociation constants (pKa = 4.76 and 6.40) and forms mono- and basic salts. There are some literature data that

show a third dissociation constant for the hydroxyl groups present at the middle carbon of citric acid in a strongly basic solution with a pKa of 13.0 [28]. The formation of negative charge on the oxygen of carboxylate part of citric acid encourages the attraction of these negative charges with lead ions enhance the removal of Pb(II) as shown in Fig. 3.17.

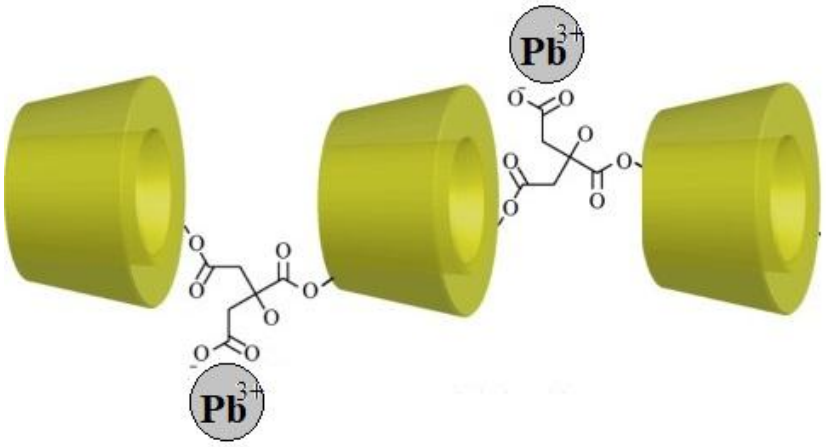


Figure 3.17: Dissociation of citric acid in polymer B.

The capability of polymer (A) to remove ferric ions from its Iron (III) chloride aqueous solution was examined. The result of this batch experiment is shown in Table 3.11.

Table 3.11: Fe^{3+} removal efficiency for polymer (A) under optimum conditions

Iron (III) chloride conc. (mg/L)	The residual [Fe^{3+}] (mg/L)	% Removal
50	26.9	46.2%

The capability of polymer (B) to remove chromic ions from its chromic chloride aqueous solution was examined. The result of this batch experiment is shown in Table 3.12.

Table 3.12: Cr^{3+} removal efficiency for polymer (B) under optimum conditions

Chromic chloride conc. (mg/L)	The residual [Cr^{3+}] (mg/L)	% Removal
50	11.8	76.3%

3.5 Isotherm lead ions removal

To examine the relationship between the amount of lead ions uptake at equilibrium (q_e) and aqueous concentrations of lead ions (C_e) at equilibrium; Langmuir and Freundlich models were used in the data analysis [54].

3.5.1 Langmuir Isotherm

Regarding to the terms shown in equation 3.1, q_m and K_L they were calculated from the slope and the intercept of the Langmuir plot of C_e/q_e vs. C_e. From Figure 3.18 represents the Langmuir plot, the amount adsorbed for monolayer formation (q_m), Langmuir adsorption-desorption equilibrium constant (K_L) and regression constant (R^2) were determined and values are shown in Table 3.13.

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \qquad (3.1)$$

Where:

C_e= the concentration of the adsorbed substance at equilibrium (mg/L), here is lead ions

q_e= the amount of adsorbed substance (here lead ions) uptake at equilibrium (mg/g)

q_m= Maximum capacity of monolayer coverage (mg/g)

K_L= Langmuir isotherm constant (L/mg)

The main feature of Langmuir adsorption isotherm parameter could be used to estimate the affinity between the adsorbate and the sorbent using an equilibrium parameter (R_L), which is shown in the following relationship [55]:

$$R_L = \frac{1}{(1+K_L C_o)} \quad (3.2)$$

Where C_o is the maximum initial concentration

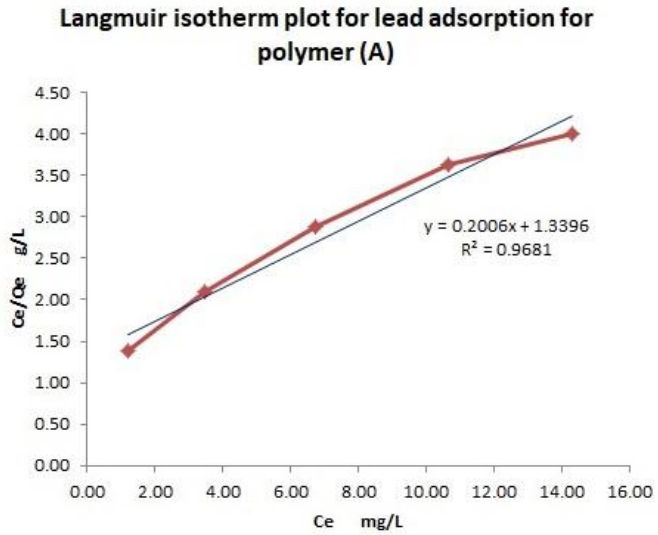


Figure 3.18: Langmuir plot for lead ions removal on polymer A. (Temp.= 30°C, pH= 8.8, time= 30 min., Volume= 10 mL, polymer dose= 0.1 g)

Table 3.13: Correlation coefficient and parameters of Langmuir isotherm model for removal of Pb(II) by polymer A.

Langmuir isotherm model parameters				
Adsorbate	Parameters			
	Q_m (mg/g)	**K_L= (L/mg)**	**R_L**	**R^2**
Polymer (A)	4.99	0.15	0.118	0.9681

Calculations were done for polymer (B), and the results are presented in Figure 3.19 and Table 3.14.

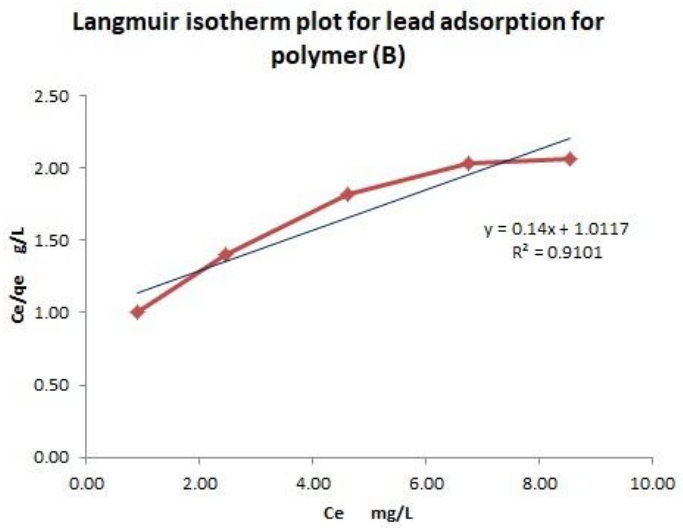


Figure 3.19: Langmuir plot for lead ions removal on polymer (B). (Temp.= 30°C, pH= 8.8, time= 30 min., Volume= 10 mL, polymer dose= 0.1 g)

Table 3.14: Parameters and correlation coefficient of Langmuir isotherm model for removal onto polymer (B).

Langmuir isotherm model parameters				
Adsorbate	Parameters			
	Q_m (mg/g)	**K_L= (L/mg)**	**R_L**	**R^2**
Polymer (B)	7.14	0.14	0.125	0.9101

3.5.2 Freundlich Isotherm

The Freundlich isotherm is used for characterize of heterogeneous systems. The isotherm is represented by the following equation:

$$\ln q_e = \frac{1}{n} ln\ C_e + lnK_F \qquad (3.3)$$

where K_f and n are Freundlich constants that correspond to removal capacity and removal intensity, respectively which can be determined from the plot of ($ln\ q_e$) versus ($ln\ C_e$) [55].

Freundlich constants K_F and n and regression constant (R^2) were determined for polymer (A) and polymer B; data are shown in Tables 3.15 and 3.16 which were calculated from figures 3.20 and 3.21 respectively:

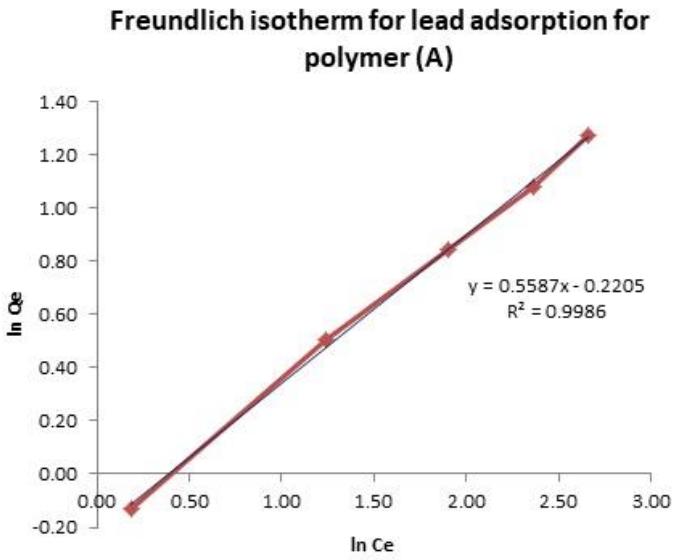


Figure 3.20: Freundlich plot for lead ions removal on polymer (A). (Temp.= 30^{o}C, pH= 8.9, time= 30 min., Volume= 10 mL, polymer dose= 0.1 g)

Table 3.15: Correlation coefficient and parameters and of Freundlich isotherm model for removal of lead ions by polymer (A).

Freundlich isotherm model parameters				
Adsorbate	Parameters			
	1/n	**n**	**K_F= (mg/g (L/mg)$^{1/n}$)**	**R^2**
Polymer (A)	0.5587	1.79	0.802	0.9986

For polymer (B), the results are presented in Figure 4.17 and Table 4.16.

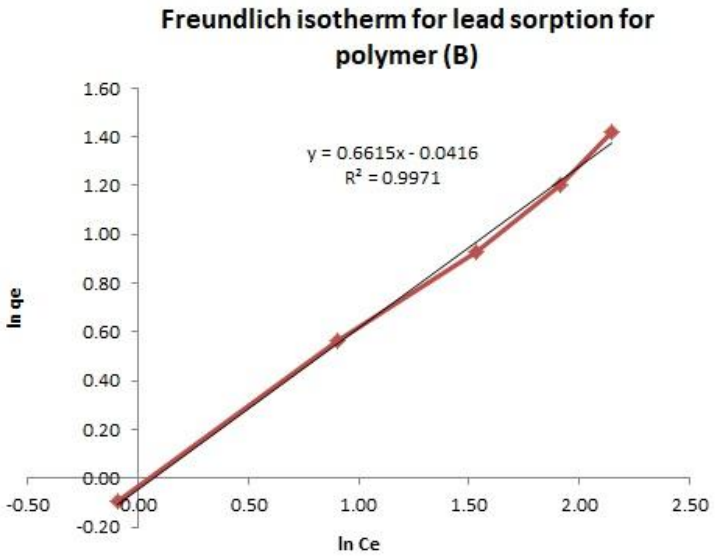


Figure 3.21: Freundlich plot for lead ions removal on polymer (B). (Temp.= 30°C, pH= 8.9, time= 30 min., Volume= 10 mL, polymer dose= 0.1 g)

Table 3.16: Parameters and correlation coefficient of Freundlich isotherm model for removal of lead ions by polymer (B).

Freundlich isotherm model parameters				
Adsorbate	Parameters			
	1/n	**n**	**K_F= (mg/g (L/mg)$^{1/n}$)**	**R^2**
Polymer (B)	0.6615	1.51	0.96	0.9971

From Langmuir isotherm data in tables 3.13 and 3.14 the values of R_L were found to be 0.118 and 0.125 at 30°C for polymer (A) and polymer (B) respectively which indicate that the adsorption of lead ions on the prepared polymers is favorable and R^2 values are 0.9681 and 0.9101 for polymer (A) and polymer (B) respectively. From Freundlich isotherm data in tables 3.15 and 3.16; value of 1/n = 0.5587 while n=1.79 for polymer (A) and value of 1/n = 0.6615 while n=1.51 for polymer (B), pointing that the adsorption of lead ions on the prepared polymers is favorable and the R^2 values are 0.9986 for polymer (A) and 0.9971 for (B).

Greater value of n which means low value of 1/n and indication of a stronger interaction among sorbent and adsorbate. The 1/n value between 0 and 1, the value indicates a more heterogeneous when 1/n becomes closer to zero [49]. Freundlich adsorption model showed the greatest value of regression and therefore the most convenient.

3.6 Kinetics of lead ions removal process

The rate constant for the removal of lead ions from an aqueous solution by polymers A and B was determined based on the pseudo first-order equation (Lagergren equation):

$$ln(q_e - q_t) = lnq_e - k_1 t \qquad (3.4)$$

Where q_e is the adsorption capacity of the adsorbent polymer at equilibrium (mg/g), q_t is the amount of lead ions adsorbed as a function of time t (mg/g) and K_1 is the pseudo first order rate constant (min^{-1}) [56].

A graph of $\ln(q_e - q_t)$ vs. time was plotted to obtain the pseudo first order rate constant for polymer (A) as shown in Figure 3.22.

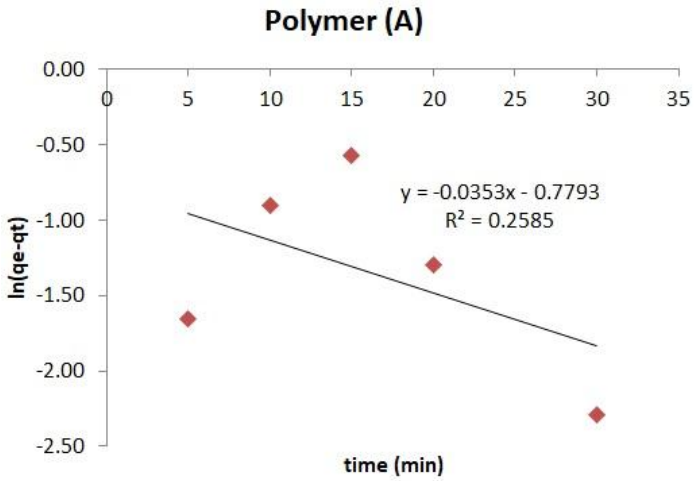


Figure 3.22: Pseudo first order removal kinetics of lead ions by polymer (A). (Temp.= 30°C, pH= 9, Volume= 10 mL, dose= 0.1 g)

As shown in Figure 3.22, the line was nonlinear at low correlation coefficient, this means that Lagergren equation is unsuitable to lead ion removal by polymer A, so the adsorption process is not a pseudo first order. The Lagergren first order rate constant K_1, q_e and the correlation coefficient R^2 are given in Table 3.17. The calculated value of q_e didn't match the experimental value of q_e as shown in Table 3.17. This means that, the removal process of lead ions didn't obey the first-order kinetics [49][57].

The linear equation (3.5) represents the Pseudo second order adsorption reaction model [58]:

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{K_2 q_e^2} \qquad (3.5)$$

Where q_e (mg/g) and q_t (mg/g) are the adsorbate amount adsorbed at equilibrium and as a function of time t (min), respectively and K_2 (g/mg min) is the Pseudo second order equation constant rate.

The results for polymer A show that the pseudo second order kinetic model could be more appropriate. The linear regression coefficient equals 0.9935 as shown in Figure 3.23. q_e experimental and q_e calculated values for the pseudo second order model were summarized in Table 3.17. The results showed an agreement between q_e experimental and q_e calculated values for the pseudo second order model. Also, K_2 was greater than K_1. So, the pseudo second order model well represent the removal kinetics of the current systems.

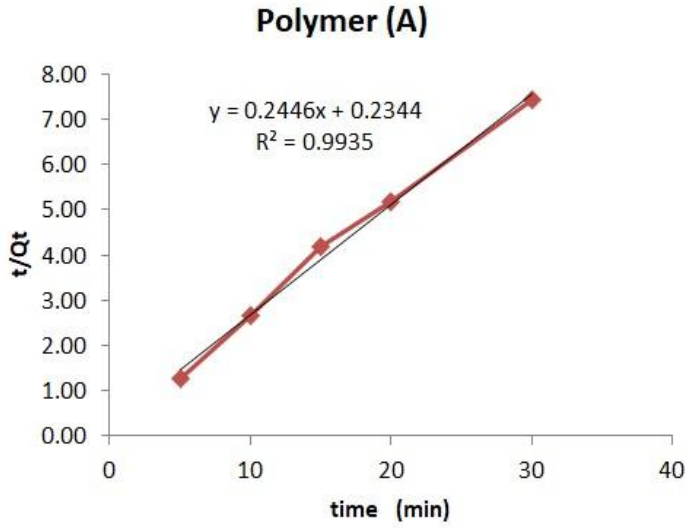


Figure 3.23: Pseudo second order removal kinetics of lead ions by polymer (A). (Temp.= 30°C, pH= 9, Volume= 10 mL, dose= 0.1 g)

Table 3.17: Pseudo first order and second order removal kinetics of lead ions by polymer (A). (Temp.= 30°C, pH= 9, Volume= 10 mL, dose= 0.1 g)

Adsorbent	$q_{e\ (exp)}$ (mg/g)	Pseudo first order			Pseudo second order		
		K_1 (min^{-1})	$q_{e\ (calc)}$ (mg/g)	R^2	K_2 (g/mg min)	$q_{e\ (calc)}$ (mg/g)	R^2
Polymer (A)	4.14	3.53×10^{-2}	0.46	0.2585	0.255	4.09	0.9935

All of the previous procedures and calculations were applied using polymer (B), and the results were very similar with those related to polymer (A). Results relating to polymer (B) are represented and summarized in Fig. 3.24, Fig. 3.25 and Table 3.18

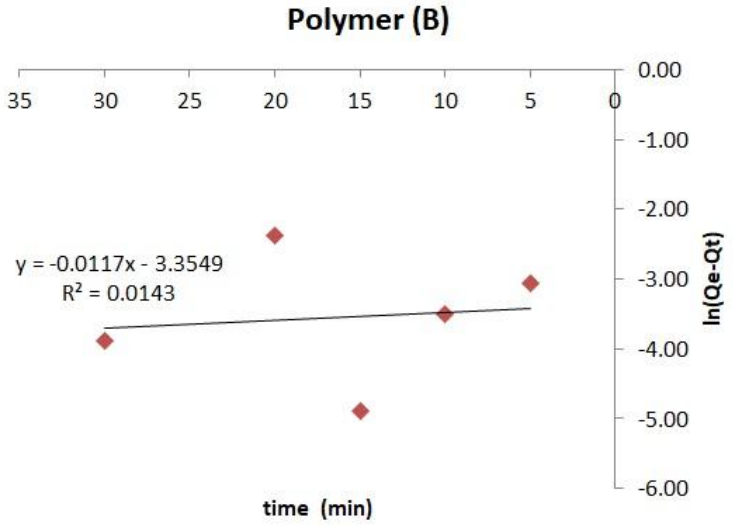


Figure 3.24: Pseudo first order removal kinetics of lead ions by polymer (B). (Temp.= 30°C, pH= 9, Volume= 10 mL, dose= 0.1 g)

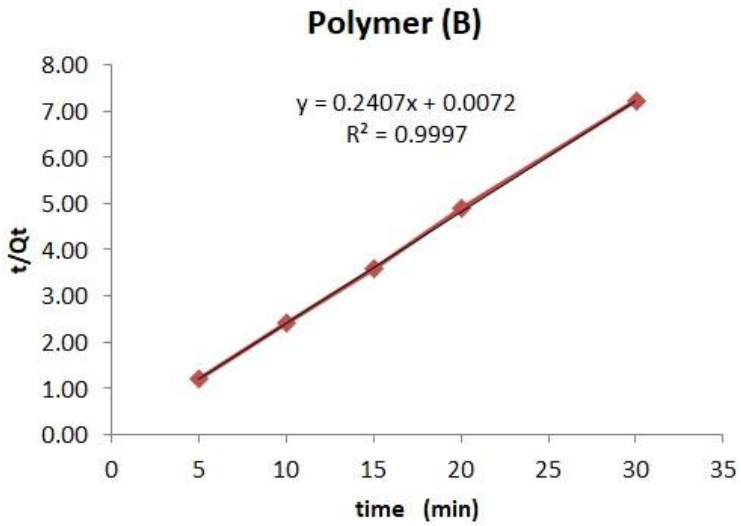


Figure 3.25: Pseudo second order removal kinetics of lead ions by polymer (B). (Temp.= 30°C, pH= 9, Volume= 10 mL, dose= 0.1 g)

Table 3.18: Pseudo first order and second order removal kinetics of lead ions by polymer (B). (Temp.= 30°C, pH= 9, Volume= 10 mL, dose= 0.1 g)

Adsorbent	$q_{e\ (exp)}$ (mg/g)	Pseudo first order			Pseudo second order		
		K_1 (min^{-1})	$q_{e\ (calc)}$ (mg/g)	R^2	K_2 (g/mg min)	$q_{e\ (calc)}$ (mg/g)	R^2
Polymer (B)	4.19	1.17×10^{-2}	0.035	0.0143	7.911	8.85	0.9997

The removal kinetics of Pb(II) by both polymer B and polymer A, follows the pseudo second order model.

3.7 Wastewater purification from metals

In general, polymer B was proved to be a good adsorbent for many metals in sewage water at pH 7 & 10, but it was noticed that results at pH 10 are better than at pH 7 that probably due to adsorption sites are more.

A sample of wastewater collected form sewer was treated with polymer B. A photo of the wastewater sample before and after treatment is shown in Figure 3.26. The metal content of the sample before purification and after are summarized in Table 3.19. The results show that, the polymer B has excellent efficiency toward most of the metals present in the wastewater sample, the removal exceeded 90% for several of them.

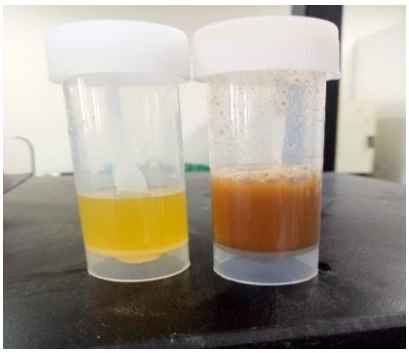


Figure 3.26: Images of waste water sample before and after treatment with the prepared polymer

Table 3.19: Metal concentration (ppm) of the wastewater before and after treatment at pH 6.5 using polymer B

Metal ion	**Ag**	**Al**	**Pb**	**Cu**	**Cd**	**Cr**	**Co**	**Fe**	**Ga**
Before	38.1	4680	12.5	103	0.67	523	12.5	8156	2.4
After	0.0006	0.0567	0.0136	0.0094	0.0001	0.0335	0.0007	0.3675	0.0003
Removal (%)	99.99	99.99	99.89	99.99	99.98	99.99	99.99	99.99	99.98
Metal ion	**Rb**	**Li**	**Mn**	**Mo**	**Ni**	**Sr**	**Cs**	**V**	**Zn**
Before	35.4	6.7	167	9.7	43	609	0.31	16	696
After	0.0202	0.005	0.0065	0.0019	0.0063	0.1208	0.0001	0.0033	0.0658
Removal (%)	99.94	99.92	99.99	99.98	99.98	99.98	99.96	99.97	99.99

Samples of wastewater were collected from different wastewater pools in the northern governorates of the West Bank. The concentrations of metal ions (ppm) in the wastewater sample were identified before and after treatment at pH 6.5 using polymer A. The results are shown in Table 3.20.

Table 3.20: Metal concentration (ppm) of the wastewater before and after treatment at pH 6.5 using polymer A

Metal ion	**Ag**	**Al**	**Pb**	**Cu**	**Cd**	**Cr**	**Co**	**Fe**	**Ga**
Before	38.1	4680	12.5	103	0.67	523	12.5	8156	2.4
After	0.0007	0.0752	0.0178	0.0121	0.0002	0.0377	0.0011	0.5183	0.0005
Removal (%)	99.99	99.99	99.85	99.98	99.97	99.99	99.99	99.99	99.97
Metal ion	**Rb**	**Li**	**Mn**	**Mo**	**Ni**	**Sr**	**Cs**	**V**	**Zn**
Before	35.4	6.7	167	9.7	43	609	0.31	16	696
After	0.0248	0.0047	0.0172	0.0028	0.0085	0.2069	0.0001	0.0039	0.1455
Removal (%)	98.79	99.92	99.98	99.97	99.98	99.96	99.95	99.97	99.97

Conclusions and Recommendations

Conclusions:

1. Cross-linked β-cyclodextrin (co-β-CyDe-CA) was synthesized using citric acid. Two polymers were prepared (A & B). The same procedure was used for the preparation of the two polymers. The only difference was the amount of citric acid was three times the amount of β-cyclodextrin in polymer (B), while the quantities were equals in polymer (A).

2. The prepared polymers were used successfully for adsorption of Pb(II) and other toxic metals from wastewater. Removal of the heavy metal ions from waste water by (co-β-CyDe-CA) reached about 98.79 to 99.99 % by both polymers.

3. It was found that removal of Pb(II) and other toxic metals from aqueous solution using the prepared polymers obey Freundlich model.

4. Results show that, Lagergren equation could be improper to describe the kinetic removal of Pb(II) by both polymers A and B. The removal process was not a pseudo first order. However it was determined that the removal process follow the pseudo second order kinetics.

5. Results show that there were no significant differences in the behavior of the two polymers A and B regarding metal adsorption. However, polymer B showed a slightly higher ability to remove toxic metal ions from waste

wastewater. This could be due to the presence of higher amount of citric acid, which allow the presence of more binding sites.

Recommendations:

1. More investigation is required to discuss the mechanism of removing metal ions by (co-β-CyDe-CA).

2. Further investigation is needed to study removal of toxic metal ions by (co-β-CyDe-CA) other than those that were used in this study.

3. Further study about the economic feasibility of the prepared polymers.

4. Studying the difference in structure if it exists between polymer (A) and polymer (B).

5. This polymer can be investigated in various applications in different areas of drug administration and the pharmaceutical industry.

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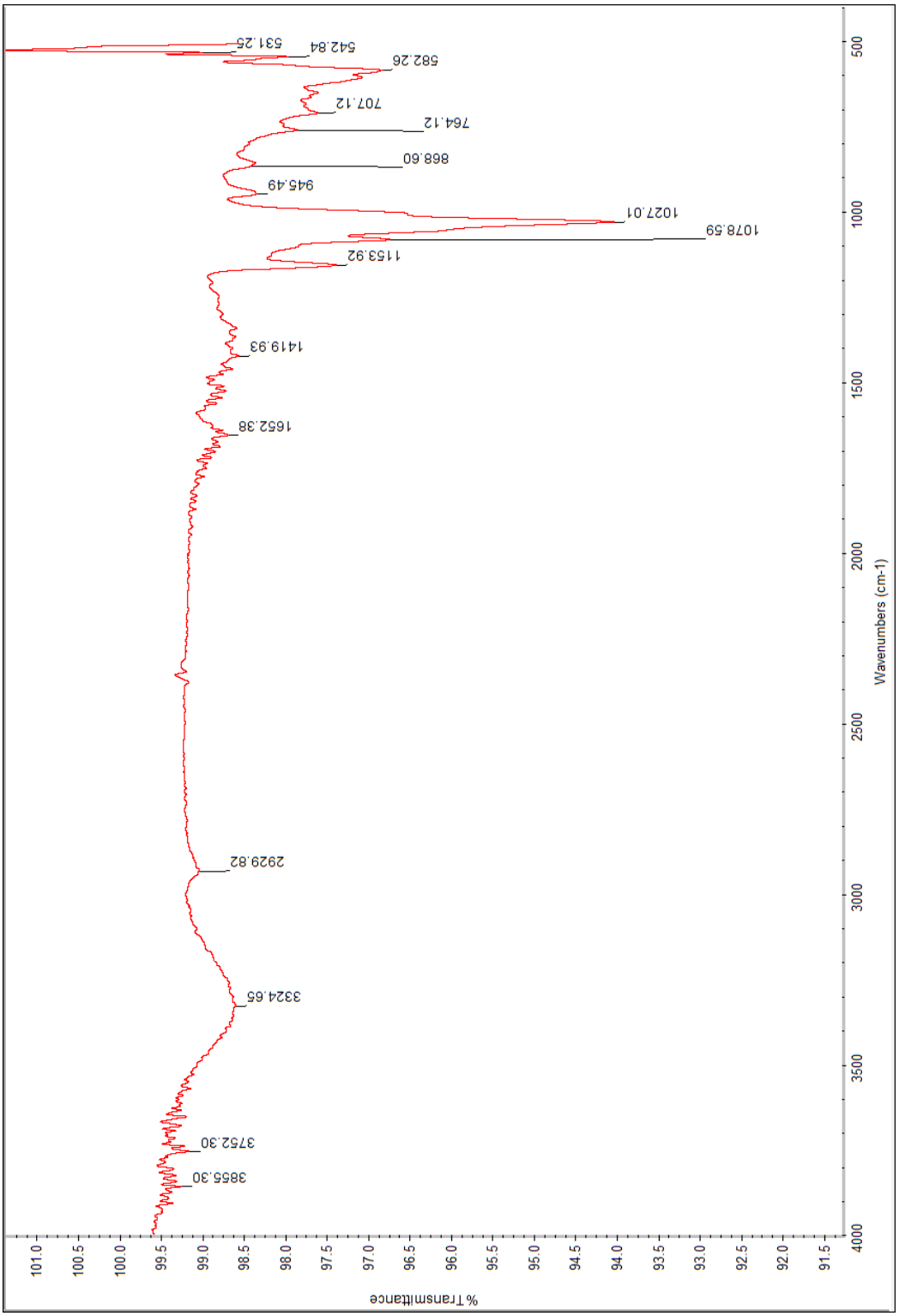
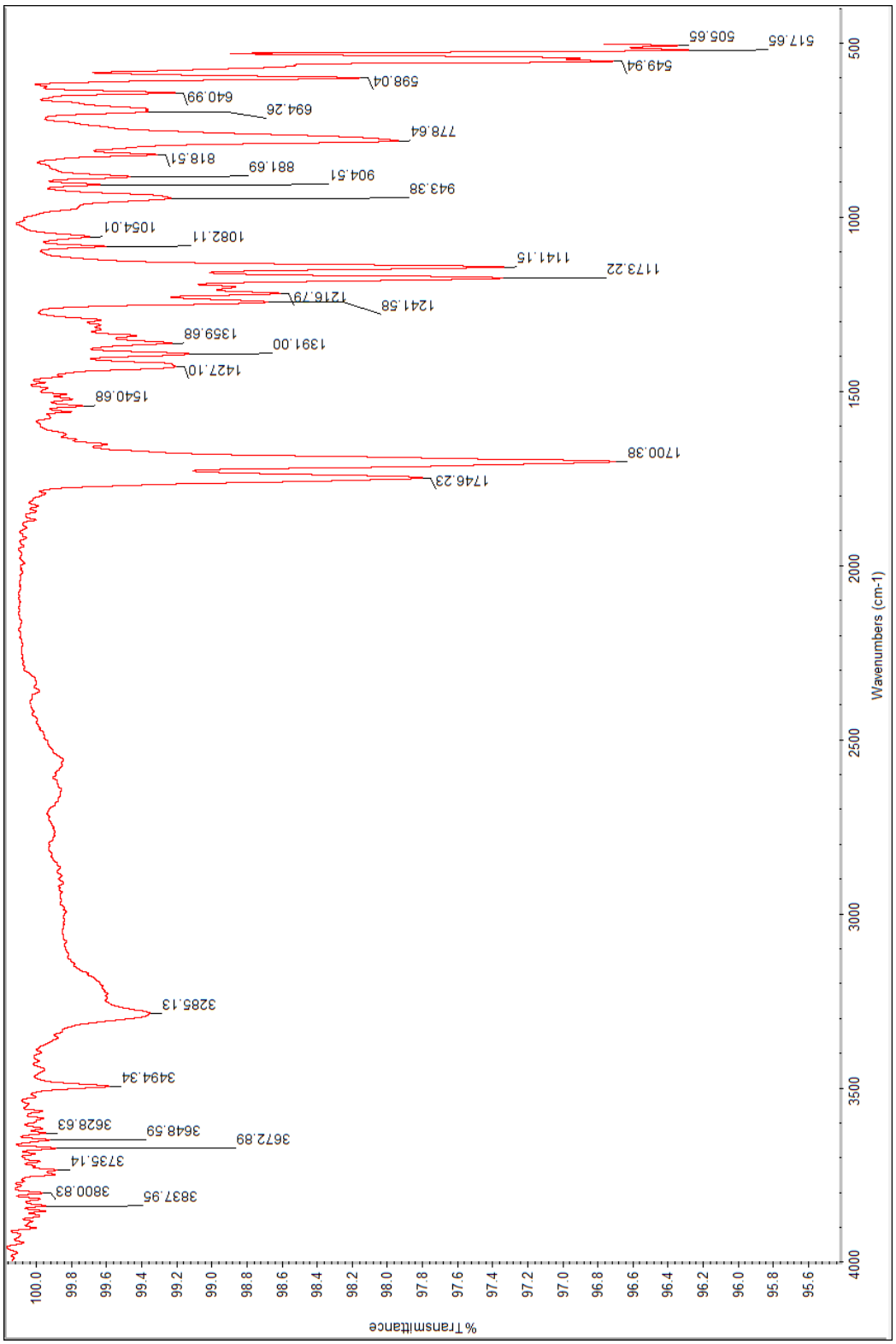
Appendix

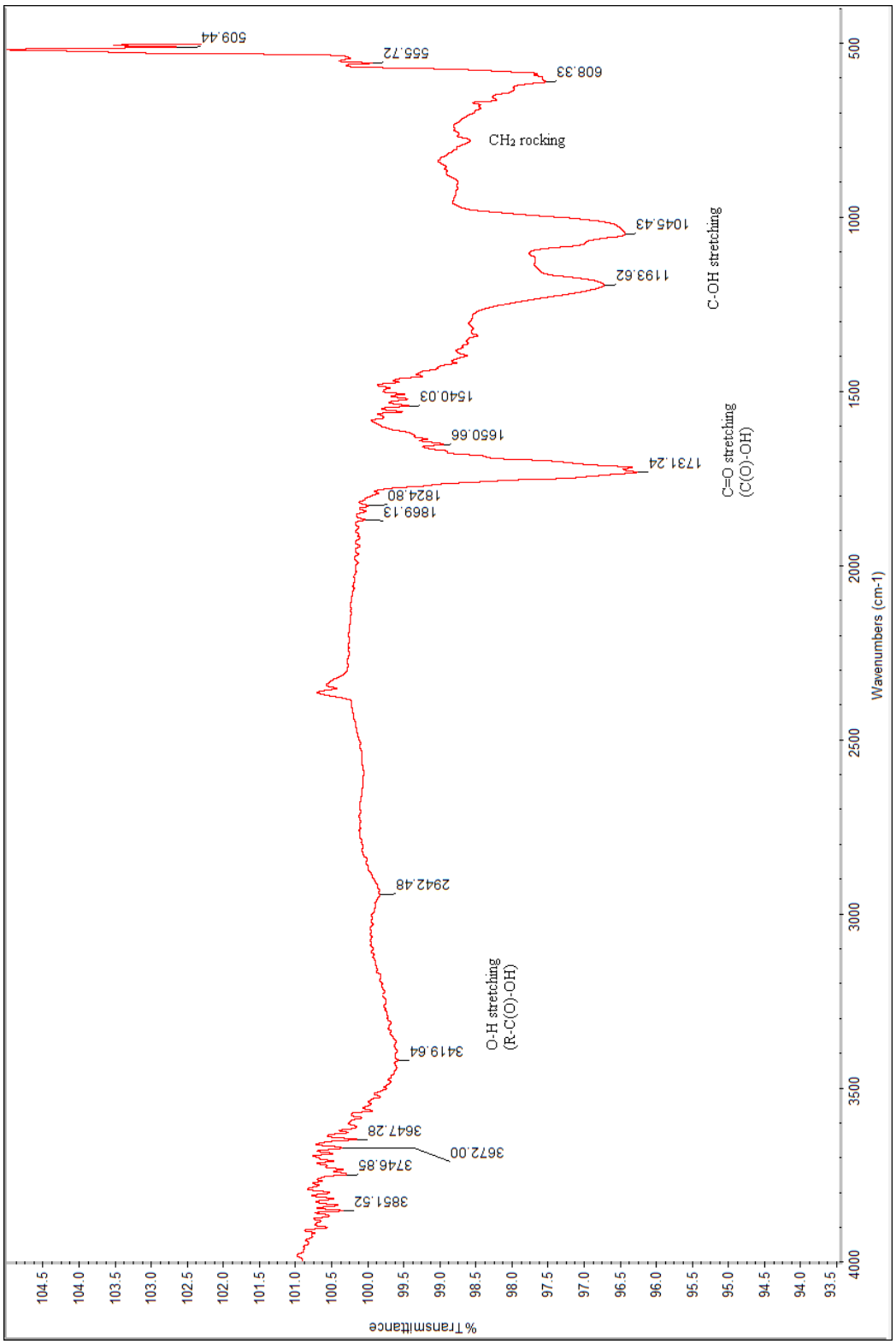
A.1: FT-IR spectra of β-Cyclodextrin



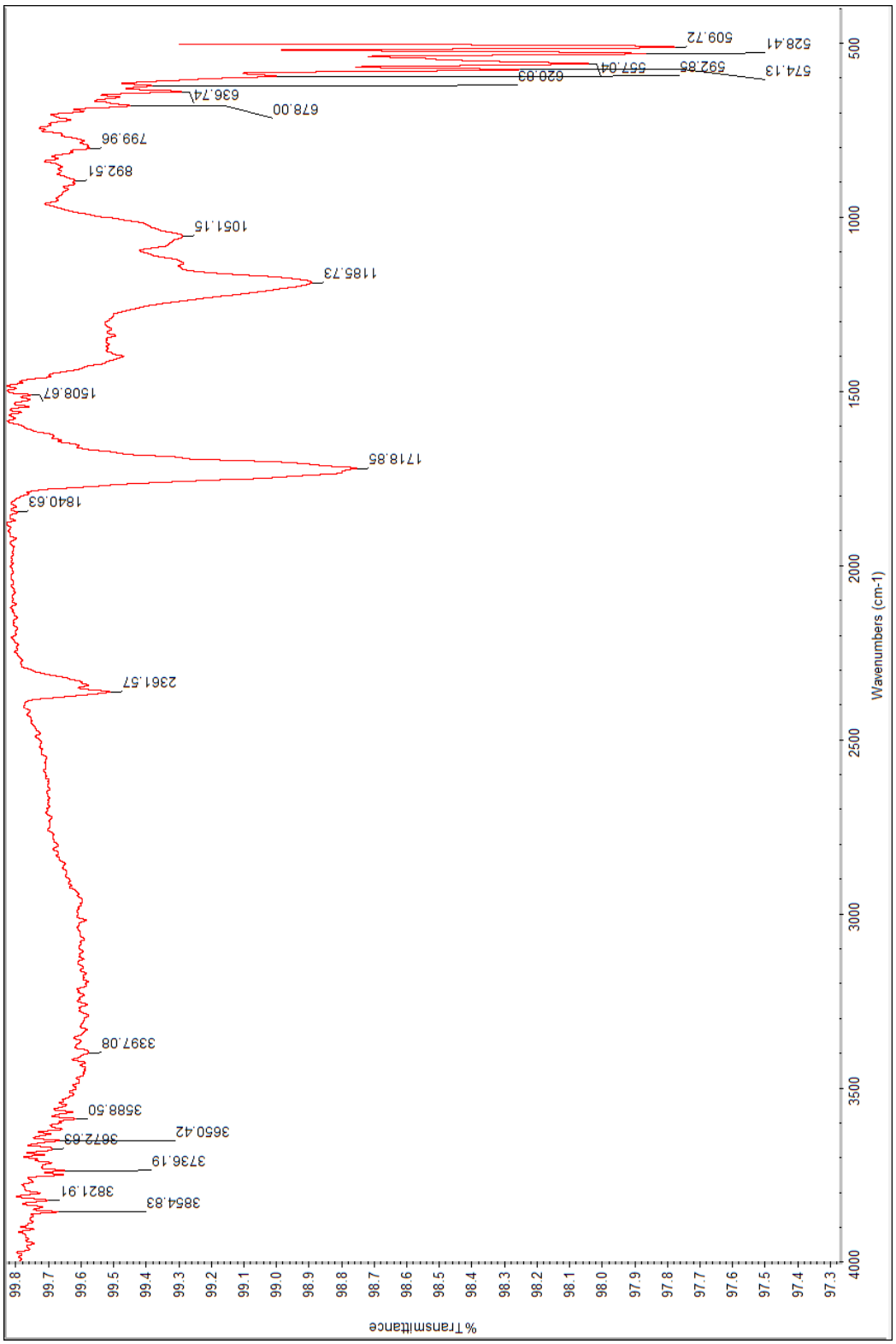
A.2: FT-IR spectra of Citric acid



A.3: FT-IR spectra of polymer (A)



A.4: FT-IR spectra of polymer (B)



A.5: Metal concentration (ppm) of the wastewater before and after treatment at pH 6.5 using polymer A:

Metal ion	Ag	Al	Pb	Cu	Cd	Cr	Co	Fe	Ga	Rb	Li	Mn	Mo	Ni	Sr	Cs	V	Zn
Befor	38.1	4680	12.5	103	0.67	523	12.5	8156	2.4	35.4	6.7	167	9.7	43	609	0.31	16	696
After	0.0007	0.0752	0.0178	0.0121	0.0002	0.0377	0.0011	0.5183	0.0005	0.0248	0.0047	0.0172	0.0028	0.0085	0.2069	0.0001	0.0039	0.1455
Removal(%)	99.99	99.99	99.85	99.98	99.97	99.99	99.99	99.99	99.97	98.79	99.92	99.98	99.97	99.98	99.96	99.95	99.97	99.97

A.6: Metal concentration (ppm) of the wastewater before and after treatment at pH 6.5 using polymer B:

Metal ion	Ag	Al	Pb	Cu	Cd	Cr	Co	Fe	Ga	Rb	Li	Mn	Mo	Ni	Sr	Cs	V	Zn
Befor	38.1	4680	12.5	103	0.67	523	12.5	8156	2.4	35.4	6.7	167	9.7	43	609	0.31	16	696
After	0.0006	0.0567	0.0136	0.0094	0.0001	0.0335	0.0007	0.3675	0.0003	0.0202	0.0050	0.0065	0.0019	0.0063	0.1208	0.0001	0.0033	0.0658
Removal(%)	99.99	99.99	99.89	99.99	99.98	99.99	99.99	99.99	99.98	99.94	99.92	99.99	99.98	99.98	99.98	99.96	99.97	99.99

جامعة النجاح الوطنية

كلية الدراسات العليا

استخدام بيتا سيكلودكسترين المترابط تصالبيًا لإزالة المعادن السامة من المياه العادمة

إعداد

رشا وليد بوريني

إشراف

أ. د. عثمان حامد

أ. د. شحدة جودة

قُدّمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في الكيمياء، بكلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس- فلسطين

2019

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الملخص

المياه هي إحدى الموارد الأساسية المتجددة المهمة للحفاظ على جميع أشكال الحياة. الأنشطة البشرية لها تأثير سلبي على المسطحات المائية. يحدث تلوث المياه عندما يتم إدخال المواد الكيميائية أو المواد الغريبة الخطرة إلى الماء. تعد الحاجة إلى الحفاظ على بيئة أنظف لبقاء الحياة المائية والبرية مهمة للغاية والتي تستحوذ بشكل متزايد على اهتمام علماء البيئة. أخطر مشكلة هي التلوث البيئي للمعادن الثقيلة والأملاح المعدنية في المياه العادمة. إن إزالة المعادن السامة من مياه الصرف الصحي أمر ضروري لأنها تؤثر وتعطل العمليات الحيوية لإنسان والكائنات الحية الأخرى باعتبارها ملوثات غير قابلة للتحلل.

بيتا سايكلوديكسترين (CyD) هو قليل السكاريد الحلقي يتكون من 7 وحدات غلوكوبرانوز مرتبطة بواسطة روابط جليكوسيدية، وهو مركب قابلة للذوبان في الماء وذو أداء عالٍ لامتصاص المواد العضوية. في هذا العمل ، تم تعديل بيتا سيكلودكسترين ليكون غير قابل للذوبان في الماء واستخدامه في تنقية المياه العادمة. سيتم تنفيذ الربط التشابكي بين جزيئات بيتا سيكلودكسترين عن طريق تفاعله مع حمض الستريك متعدد الكربوكسيل، مما يضيف إليه مجموعات وظيفية جديدة وهي مجموعات الكربوكسيل. يعد بيتا سيكلودكسترين المعدل (co-β-CyDe-CA) بوليمرًا جيدًا لاستخدامه في تنقية المياه العادمة من المعادن السامة والمواد العضوية على حد سواء. تم تحضير بوليمر (co-β-CyDe-CA) بطريقتين A و B . تم اتباع نفس الإجراءات لإعداد البوليمرين؛ والفرق الوحيد هو أن كمية الستريك أسيد كانت ثلاثة أضعاف كمية بيتا سيكلودكسترين في تحضير البوليمر (B)، في حين كانت الكميات متساوية في تحضير البوليمر(A).

تم تحضير البوليمر الجديد (co-β-CyDe-CA) بنجاح. وتؤكد نتائج على تكوين البوليمرات A و B. وقد أجريت تجارب إزالة أيونات المعادن السامة تحت نطاق واسع من pH، جرعة البوليمر، درجة الحرارة، التركيز الابتدائي ووقت الاتصال. تم تحقيق كفاءة إزالة أكثر من 98٪ من البوليمرات المعدة بعد ساعة تقريبًا، عند درجة الحموضة حوالي 9 ودرجة الحرارة حوالي 30 درجة مئوية باستخدام 0.1 غرام من البوليمر المحضر و 10 مل من محلول أيونات الرصاص المائي بتركيز أولي 50 ملغ/لتر. أظهرت النتائج التجريبية أن (co-β-CyDe-CA) كان قادرًا على إزالة أيونات الرصاص بسرعة خلال الدقائق الخمس الأولى مع كفاءة إزالة عالية تحت الظروف القلوية وحول درجة حرارة الغرفة.

لقد وجد أن إزالة أيونات المعادن السامة من المحلول المائي باستخدام البوليمرات المحضرة تم وصفها بشكل جيد بواسطة نموذج فريندليخ (Freundlich)، حيث يصف هذا النموذج الامتزاز على الأسطح غير المتجانسة التي تمتلك مواقع امتزاز ذات ارتباطات مختلفة.

يمكن وصف إزالة أيونات المعادن السامة باستخدام البوليمرات المعدة بنموذج الدرجة الثانية. نموذج الرتبة الثانية يمثل بشكل جيد ديناميكية الإزالة لكل من البوليمر (B) ، والبوليمر (A). كانت قيمة (q_e (calc.) التي تم الحصول عليها بواسطة هذا النموذج متوافقة مع قيمة (q_e (exp.) التي تشير إلى أن الامتزاز ينطوي على تفاعل كيميائي بين التجاويف البينية للبوليمر المعد وأيونات المعادن الثقيلة، والتي قد تكون الخطوة المحددة لمعدل سرعة التفاعل حيث يكون الربط التشابكي بين جزيئات بيتا سيكلودكسترين فعل تعاوني بين تجاويف (co-β-CyDe-CA) والمكونات القابلة للذوبان في الماء، حيث تتشارك قوى التكافؤ بين هذه التجاويف وأيونات المعادن.